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## **Methods for Tier 2 Modeling within the Training Range Environmental Evaluation and Characterization System**

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Jeffrey A. Gerald

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**Abstract:** The Training Range Environmental Evaluation and Characterization System (TREECS) is being developed for the Army. This system has varying levels of capability to forecast the fate and risk of munitions constituents (MC) (such as high explosives (HE)), within and transported from firing/training ranges to surface water and groundwater. The overall objective is to provide Army environmental specialists with tools to assess the potential for MC migration into surface water and groundwater systems and to assess range management strategies to protect human and environmental health. Tier 2 will consist of time-varying contaminant fate/transport models for soil, vadose zone, groundwater, and surface water to forecast MC export from ranges and resulting concentrations in receiving waters. Model results can be used to assess the potential for surface water and/or groundwater MC concentrations to exceed protective health benchmarks at receptor locations of interest.

The Tier 2 models do not make the highly conservative assumptions of steady-state (time-invariant) conditions and no MC loss or degradation was used for Tier 1. Thus, media concentrations computed with Tier 2 should be closer to those expected under actual conditions. Media concentrations will also reflect time phasing associated with time-varying MC loading conditions and transport arrival times, which can be greatly extended for the vadose zone and groundwater. Having time as a dimension in the analysis provides a powerful tool for examining range management strategies to promote attenuation of media concentrations.

The information provided in this report is sufficient to serve as design specifications for the development of models and software that will comprise Tier 2 of TREECS. The details of the Tier 2 soil model formulations provided herein can also help serve as documentation for that model. All components will be packaged within a user-friendly PC client-based application with an emphasis on ease-of-use.

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## **Preface**

This study was funded by the U.S. Army's Environmental Quality and Installations (EQI) Research Program. This report was prepared by Dr. Mark Dortch of MSD Engineering Consulting, which was under contract to the U.S. Army Engineer Research and Development Center (ERDC), and Dr. Billy Johnson of the Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL) of ERDC. Dr. Zhonglong Zhang of SpecPro, Inc., a company under contract to EPED, coded and tested the soil model formulations. Additionally, Mr. Jeffrey Gerald of WQCMB provided many technical suggestions during the study's development. Staff of the U.S. Army Environmental Command (AEC) and the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) provided technical review of this report.

The study was conducted under the general direction of Dr. Beth Fleming, Director of the EL; Dr. Richard Price, Chief, EPED; and Dr. Quan Dong, Chief, WQCMB. Dr. John Cullinane was Director of the EQI Program.

Drs. James R. Houston and Jeffery P. Holland were Directors of ERDC during this study. COL Kevin J. Wilson was Commander and Executive Director.



## Unit Conversion Factors

Multiply	By	To Obtain
cubic feet	0.02831685	cubic meters
degrees Fahrenheit	$(F-32)/1.8$	degrees Celsius
feet	0.3048	meters
miles (U.S. statute)	1,609.347	meters
pounds mass	453.59	grams
slugs	14.59390	kilograms
square feet	0.09290304	square meters

# List of Acronyms, Abbreviations, and Symbols

## Acronyms and Abbreviations

AEC	Army Environmental Command
AOI	area of interest
ARCDB	Army range constituent database
CHPPM	Center for Health Promotion and Preventive Medicine
CMS	Contaminant Model for Streams
Comp B	Composition B, a high explosive with a mixture of RDX and TNT
CR	Crank-Nicolson solution method
CSM	conceptual site model
CSTR	continuously stirred tank reactor
DODIC	Department of Defense Identification Code
EL	Environmental Laboratory
EPED	Environmental Processes and Effects Division
ERDC	Engineer Research and Development Center
FRAMES	Framework for Risk Analysis in Multimedia Environmental Systems
HCB	hexachlorobenzene
HGCT	Hydro-Geo-Characteristics toolkit
HE	high explosives
HMX	High melting explosive, a high explosive
ISS	inorganic suspended solids
L	length
M	mass
MC	munitions constituents
MEPAS	Multimedia Environmental Pollutant Assessment System
MIDAS	Munitions Items Disposition Action System
MW	molecular weight
NSN	National Stock Number
Octol	a high explosive that is mixture of HMX and TNT
OM	organic matter
ORAP	Operational Range Assessment Program
Plus-SG	Plus operator for Surface water and Groundwater
RDX	Research Department Explosive, a high explosive
SAFRs	small arms firing ranges
SCF	soil and sediment concentration file used in FRAMES
S/U	sensitivity and uncertainty
T	time
TCE	trichloroethylene
TNT	tri-nitro-toluene, a high explosive

TREECS	Training Range Environmental Evaluation and Characterization System
Tritonal	a high explosive that is a mixture of TNT and aluminum
TSS	total suspended solids concentration
VSS	volatile suspended solids
WCF	water concentration file used in FRAMES
WFF	water flux file used in FRAMES
0D	zero-dimensional
1D	one-dimensional
3D	three-dimensional

## Mathematical Symbols

$A$	surface area of AOI, $m^2$
$A$	constant cross-sectional area of the flow for option of entering cross-sectional area for CMS, $m^2$
$AF$	particle surface area factor, dimensionless
$A_m$	mixed sediment layer surface area for RECOVERY model, $m^2$
$A_{si}$	surface area of the individual solid phase MC particle, $cm^2$
$A_w$	long-term average water surface area for RECOVERY model, $m^2$
$B$	stream constant top width for option of entering stream width and hydraulic depth for CMS, m
$a$	soil detachability due to rainfall, kg/L
$a$	parameter in the function $A = aQ^b$ for option of entering a function for cross-sectional area as related to flow for CMS
$b$	soil type coefficient for the MEPAS groundwater model, which is an empirical parameter relating soil matric potential and moisture content and is dependent on soil texture, dimensionless
$b$	parameter in the function $A = aQ^b$ for option of entering a function for cross-sectional area as related to flow for CMS
$C$	dissolved constituent concentration in vadose zone pore water and aquifer for the MEPAS groundwater model, mg/L
$C_a$	concentration of MC adsorbed to soil particles, $M_p/M_{soil}$ , mg/kg
$C_{bi}$	initial constituent concentration in the sediment bed for CMS, mg/kg
$C_e$	instantaneous soil pore-water chemical concentration in the rainfall-extraction exchange layer during a rainfall event, $g/m^3$

$C_i$	constant constituent background concentration in stream at the head of the reach for CMS, mg/L
$\bar{C}_e$	rainfall event's time-averaged soil-pore water chemical concentration in the soil rainfall-extraction exchange layer adjacent to the overland water, g/m <sup>3</sup>
$C_g$	vapor or gas concentration in air, $M_a/V_a$ , g/m <sup>3</sup>
$C_l$	concentration dissolved in pore water or liquid phase, $M_d/V_w$ , g/m <sup>3</sup>
$C_{la}$	chemical concentration in water adjacent to a solid phase MC particle, g/cm <sup>3</sup>
$C_m$	total (particulate and dissolved) contaminant concentration in the mixed sediment layer of the sediment bed for the RECOVERY model, g/m <sup>3</sup>
$C_{ns}(0)$	initial (at time 0) total non-solid phase MC concentration in soil on a soil mass basis, mg/kg
$C_o$	soil pore-water concentration below the rainfall-extraction exchange layer and is equal to $F_{dp}C_{tt}/\theta_w$ or $C_l$ , g/m <sup>3</sup>
$C_s$	aqueous solubility of a chemical, g/cm <sup>3</sup>
$\bar{C}_s$	precipitation temperature-weighted, average constituent solubility limit in water, g/cm <sup>3</sup>
$C_s(z)$	total (particulate and dissolved) contaminant concentration in the deep sediment layers of the sediment bed for the RECOVERY model, g/m <sup>3</sup>
$C_{tt}$	total (particulate, dissolved, and vapor) non-solid phase MC concentration within the soil matrix on a total volume basis, g/m <sup>3</sup>
$C_w$	total (particulate and dissolved) contaminant concentration in surface water for the RECOVERY model, g/m <sup>3</sup>
$c$	parameter in the function $H = cA^d$ for option of entering a function for hydraulic depth as related to flow cross-sectional area for CMS
$c_b$	concentration of the constituent in the sediment bed as total mass per total volume basis for CMS, g/m <sup>3</sup>
$c_w$	concentration of the constituent in the water column as total mass per total volume basis for CMS, g/m <sup>3</sup>
$c_{w0}$	initial contaminant concentration of constituent in water for RECOVERY model, µg/L
$D_G^{air}$	MC vapor or gas diffusion coefficient in air, m <sup>2</sup> /day
$D_{G_{eff}}$	effective diffusion coefficient for a vapor in soil, m <sup>2</sup> /day
$D_{mol}$	molecular diffusion coefficient for solute in water, cm <sup>2</sup> s <sup>-1</sup>

$\overline{D}_{om}$	rainfall mass-weighted, mean raindrop diameter for dissolution, cm
$DUD_{j,k}$	percent of duds for munitions item $j$ for year $k$
$D_w$	chemical's aqueous phase diffusion coefficient, cm <sup>2</sup> /sec
$D_x$	stream longitudinal diffusion coefficient for CMS, m <sup>2</sup> /day
$D_{x,y,z}$	dispersion coefficients in the x-, y-, and z-directions for the MEPAS groundwater model, cm <sup>2</sup> /sec
$D_z$	vadose zone and groundwater dispersion coefficient in the z direction for the MEPAS groundwater model, cm <sup>2</sup> s <sup>-1</sup>
$D_2$	diffusion coefficient for carbon disulfide in air, 0.102 cm <sup>2</sup> /sec
$d$	parameter in the function $H = cA^d$ for option of entering a function for hydraulic depth as related to flow cross-sectional area for CMS
$d_e$	soil exchange layer thickness for rainfall-extraction, m
$d_i$	average diameter of MC particles, cm
$d_s$	particle diameter in Duboy's equation, ft
$d_{sm}$	mean, initial particle diameter for solid phase MC residue input into soil model, μm
$d_v$	diffusion layer thickness for volatilization in the top of the soil layer, m
$E$	average annual soil erosion rate, m/yr
$e_r$	rate of soil pore water ejection during a rainfall event, m/sec
$F_{ap}$	factor used to convert from total concentration on a total volume basis to air concentration in the porous media on a total volume basis
$F_{db}$	factor to convert from total to dissolved constituent concentration in the sediment bed pore water for CMS, dimensionless
$F_{decay}$	MC degradation flux, g/yr
$F_{dis}$	dissolution flux, g/yr
$F_{dp}$	factor used to convert from total concentration on a total volume basis to dissolved concentration in the porous media on a total volume basis for the soil model, dimensionless
$F_{dw}$	fraction of the constituent dissolved in the water column for CMS, dimensionless
$F_e$	MC flux due to soil erosion, g/yr
$F_{es}$	erosion flux of MC solid phase particles, g/yr
$F_{if}$	fraction of annual water infiltration flow rate and mass flux that goes to soil interflow

$F_l$	MC leaching flux, g/yr
$F_{pb}$ $F_{pp}$	fraction of constituent in particulate form in the bed for CMS factor used to convert from total concentration on a total volume basis to particulate concentration in the porous media on a total volume basis
$F_{precip}$	precipitation flux of MC due to dissolved pore water concentration exceeding the water solubility limit, g/yr
$F_{pw}$	fraction of the constituent in particulate form in the water column for CMS, dimensionless
$F_r$	rain-induced pore water ejection and runoff flux of MC, g/yr
$F_{vol}$	MC volatilization flux, g/yr
$f_{MC}$	fraction by weight of solid phase MC mass to soil mass
$f_{oc}$	fraction by weight of soil organic carbon
$G$	specific gravity of a sediment particle, dimensionless
$g$	acceleration due to gravity, 32.2 ft <sup>2</sup> /sec
$H$	hydraulic depth of the stream for CMS, m
$H_e$	Henry's law constant, atm·m <sup>3</sup> /g·mol
$HO_{j,k}$	percent of high order detonations for munitions item $j$ for year $k$
$H(t)$	cumulative rainfall over time for dissolution, cm
$H_w$	long-term average of surface water mean depth for RECOVERY model, m <sup>2</sup>
$h$	boundary layer film thickness around an MC solid phase particle, cm
$h$	water layer thickness coating an explosive particle, cm
$h$	active sediment layer thickness for CMS, m
$h$	depth of flow for shear stress calculation, ft
$I$	rainfall intensity, m/sec
$\bar{I}$	average or typical rainfall intensity associated duration $\bar{T}$ , m/time
$K_d$	distribution coefficient for partitioning a constituent between soil particles and water, L/kg
$K_{dm}$	sediment-water partition coefficient for the mixed sediment layer for RECOVERY model, L/kg
$K_{ds}$	sediment-water partitioning coefficient for the constituent in the sediment bed for CMS and for deep sediments of RECOVERY model, L/kg

$K_{dw}$	sediment-water partitioning coefficient for the constituent in the water column for CMS and RECOVERY models, L/kg
$K_H$	dimensionless Henry's constant for partitioning a constituent between air and water
$K_{oc}$	organic carbon – water partition coefficient, L/kg
$K_{ow}$	constituent octanol-water partition coefficient, mg/m <sup>3</sup> octanol/ mg/m <sup>3</sup> water
$K_s$	saturated hydraulic conductivity for the MEPAS groundwater model, cm s <sup>-1</sup>
$K_v$	volatilization rate of vapor phase MC, m/yr
$K(\theta_w)$	unsaturated hydraulic conductivity for the MEPAS groundwater model, cm s <sup>-1</sup>
$k_{db}$	decay rate of dissolved constituent in bed pore water for CMS, day <sup>-1</sup>
$k_{dw}$	decay rate of dissolved constituent in the water column for CMS, day <sup>-1</sup>
$k_m$	MC decay rate for sediment mixed layer in RECOVERY model, yr <sup>-1</sup>
$k_{pb}$	decay rate of particulate constituent in the bed for CMS, day <sup>-1</sup>
$k_{pw}$	decay rate of particulate constituent in the water column for CMS, day <sup>-1</sup>
$k_s$	MC decay rate for sediment deep layers in RECOVERY model, yr <sup>-1</sup>
$k_w$	MC decay rate for water column in RECOVERY model, yr <sup>-1</sup>
$k_v$	stream volatilization rate of the constituent for CMS, m/day
$L$	total sediment bed depth to be modeled for RECOVERY model, m
$L_f$	length of the AOI, or dimension parallel to the groundwater flow, m
$L_{i,k}$	MC residue mass loading for constituent $i$ for year $k$ , g/yr
$LO_{j,k}$	percent of low order detonations for munitions item $j$ for year $k$
$L(t)$	time-varying solid phase MC mass loading, g/yr
$l$	length of a right cylindrical MC particle, cm
$M_a$	MC vapor mass in air space within soil matrix, g
$M_d$	MC mass dissolved in soil matrix pore water, g
$M_{dis}(t)$	particle mass loss over time due to dissolution, g
$M_{i,j}$	mass of constituent $i$ in munitions item $j$ delivered to impact area, g/item
$M_{ns}$	non-solid phase MC mass, g
$M_p$	MC mass adsorbed to soil particles, g

$M_s$	solid phase MC mass, g
$M_{soil}$	mass of soil in the AOI, g
$M_I$	molecular weight of the MC of interest
$M_2$	molecular weight of carbon disulfide, 76 g/mole
$m$	total solid phase MC mass for all solid phase MC particles, g
$m$	MEPAS groundwater model coefficient dependent on soil type where $m = 2b + 3$ , dimensionless
$m_i$	MC solid phase mass for particle $i$ , g
$N$	average number of rainfall events per year, events/yr
$N_{j,k}$	number of munitions item $j$ fired for year $k$
$n$	total number of munitions items used at AOI
$P$	average annual precipitation, m/yr
$P_r$	average annual rainfall, m/yr
$P_t$	average annual total precipitation, cm/yr or m/yr depending on use
$Q$	average annual water flow rate through the water body for RECOVERY model, m <sup>3</sup> /yr
$Q$	constant background stream flow rate (e.g., annual mean flow) at the head of the reach (without any flow from the AOI) for CMS, m <sup>3</sup> /yr
$Q_w$	water flow rate due to net infiltration, or percolation, from soil (groundwater recharge into vadose zone), m <sup>3</sup> /yr
$q_{bv}$	volume of bed material load per unit width in Duboy's equation, ft <sup>2</sup> /sec
$q_{bv^*}$	dimensionless volumetric unit sediment discharge
$q_r$	average annual surface water runoff rate, m/yr
$q_w$	average annual Darcy water infiltration rate, m/yr
$R$	retardation factor, dimensionless
$Re_{dQ}$	event-based runoff mass removal rate of pore water due to rain-induced ejection, g/sec
$R_u$	universal gas constant = 8.206 E-5 atm·m <sup>3</sup> /g-mol °K
$R_{fs}$	retardation factor in the saturated zone for the MEPAS groundwater model, dimensionless
$R_{fu}$	retardation factor for unsaturated zone or vadose zone for the MEPAS groundwater model, dimensionless
$S$	TSS concentration for CMS, g/m <sup>3</sup>
$S$	water surface slope, ft/ft
$S_w$	TSS input variable name for RECOVERY, g/m <sup>3</sup>
$SYM_{j,k}$	percent of sympathetic detonation of duds for munitions item $j$ for year $k$



$T$	time averaging interval for rainfall event, or the rainfall event duration, sec
$T_{1/2}$	half-life due to decay or degradation, yr
$\bar{T}$	average or typical rainfall event duration, time
$T$	water and sediment mean temperature for CMS, °C
$T_a$	ambient absolute temperature of the soil matrix, °K
$T_p$	total time period of simulation for CMS, yr
$T_{soil}$	average annual temperature of the soil matrix, °C
$T_w$	ambient water temperature for dissolution, °C
$t$	time, yr and sec
$t_d$	rain drop arrival interval for explosives dissolution, sec
$t_{90}$	time required to reached 90 percent mass loss from dissolution, yr
$U$	stream mean velocity for CMS, m/day and m/sec
$U_w$	mean wind speed for RECOVERY model, m/sec
$u$	pore water velocity in horizontal (X) direction for the MEPAS groundwater model, cm/sec
$u_c$	critical flow velocity for particle movement, ft/sec
$u^*$	shear velocity of the flow for CMS, m/sec
$V$	surface soil compartment volume of AOI, m <sup>3</sup>
$V_a$	volume of air in the AOI soil, m <sup>3</sup>
$V_b$	active sediment layer burial rate for CMS and RECOVERY models, m/day and m/sec
$V_d$	mass transfer rate across the sediment-water interface resulting from diffusion of the dissolved constituent for CMS and RECOVERY models, m/day and m/sec
$V_d$	Darcy velocity of groundwater flow, L/T
$V_l$	water layer volume coating a spherical explosive particle, cm <sup>3</sup>
$V_r$	sediment resuspension rate for CMS and RECOVERY models, m/day and m/sec
$V_s$	suspended solids settling rate for CMS and RECOVERY models, m/day and m/sec
$V_w$	volume of water in the AOI soil, m <sup>3</sup>
$W$	additional constant external loading rate of constituent for RECOVERY model, kg/yr
$W$	mean wind speed at 10 m above surface for CMS, m/sec
$w$	pore water velocity in the vertical (Z) direction of the vadose zone for the MEPAS groundwater model, cm s <sup>-1</sup>

$W_f$	width of the AOI, or dimension perpendicular to the groundwater flow, m
$X$	longitudinal coordinate for the MEPAS groundwater model
$X$	Usage location, i.e., distance downstream from the upstream boundary to the location of interest for CMS, km
$x$	longitudinal distance from the center of the AOI to the receptor well for the MEPAS groundwater model, cm
$x$	downstream distance along stream for CMS, m
$x$	particle shape index for solid phase MC particles that is input for the soil model; 1 for cylindrical and 2 for spherical, dimensionless
$Y$	lateral coordinate for the MEPAS groundwater model
$y$	lateral distance from the groundwater plume centerline to the receptor well for the MEPAS groundwater model, cm
$Y_{HOj,k}$	percent yield of munitions item $j$ due to high order detonation for year $k$
$Y_{LOj,k}$	percent yield of munitions item $j$ due to low order detonation for year $k$
$Y_{SYMj,k}$	percent yield of munitions item $j$ due to sympathetic detonation for year $k$
$Z$	vertical coordinate for the MEPAS groundwater model
$Z_A$	aquifer thickness, L
$Z_b$	surficial soil layer thickness of AOI, m
$Z_v$	vadose zone thickness, L
$z$	distance along the vertical coordinate or depth of the receptor well below the water table for the MEPAS groundwater model, cm
$z$	depth of mixed sediment layer for RECOVERY model, m
$\alpha$	average specific surface area of the solid phase MC mass, $\text{cm}^2/\text{g}$
$\alpha_x$	longitudinal dispersivity for the MEPAS groundwater model, cm
$\alpha_y$	lateral dispersivity for the MEPAS groundwater model, cm
$\alpha_z$	vertical dispersivity for the MEPAS groundwater model, cm
$a_0$	initial particle radius for dissolution, cm
$\beta$	consolidating parameter used in calculating rainfall-extraction (see Equation 27), $\text{sec}^{-1}$
$\beta_m$	MC mass dissolution flux rate, $\text{g}/\text{cm}^2\text{-sec}$

$\Delta t$	time step in the solution procedure for the Tier 2 soil model, yr
$\zeta$	MC dissolution mass transfer rate or solid phase surface removal rate, cm/sec
$\gamma$	specific weight of water, 62.4 lb/ft <sup>3</sup>
$\gamma$	consolidating parameter for dissolution parameters, $\gamma = P_r \alpha C_s$
$\gamma_s$	specific weight of sediment, dimensionless
$\kappa$	a computed parameter used in rainfall-extraction calculations (see Equation 33), dimensionless
$\lambda$	degradation or decay rate for the MEPAS groundwater model, sec <sup>-1</sup>
$\lambda_a$	degradation rate for the aqueous adsorbed MC, yr <sup>-1</sup>
$\lambda_l$	degradation rate for the liquid (aqueous dissolved) MC, yr <sup>-1</sup>
$\phi$	soil porosity or ratio of void volume to total volume; water content when water-saturated and porosity of the sediment bed for CMS, fraction
$\phi_e$	effective porosity for the MEPAS groundwater model, fraction
$\phi_m$	mixed sediment layer porosity for RECOVERY model, fraction
$\phi_s$	deep sediment porosity for RECOVERY model, fraction
$\rho_b$	soil dry bulk density, g/ml or kg/L
$\rho_s$	dry sediment particle density, kg/L
$\rho_{sm}$	solid phase constituent mass density, g/cm <sup>3</sup>
$\theta$	an empirical coefficient to account for temperature effects on dissolution rate due to changes in solubility
$\theta_f$	soil field capacity, fraction
$\theta_w$	soil volumetric moisture content or ratio of water volume to total volume, fraction
$\tau_c$	critical shear stress for particle, lb/ft <sup>2</sup>
$\tau_o$	shear stress of the water flow, lb/ft <sup>2</sup>
$\tau_w$	water residence time for RECOVERY model, yr
$\tau_*$	dimensionless Shields parameter
$\omega_o$	Rubey's clear-water sediment fall velocity, L/T

# 1 Introduction

## Background

The Training Range Environmental Evaluation and Characterization System (TREECS) is being developed for the Army. The system has varying levels of capability to forecast the fate of munitions constituents (MC) (such as high explosives (HE)) within and transported from firing/training ranges to surface water and groundwater. The overall objective is to provide Army environmental specialists with tools to assess the potential for MC migration into surface water and groundwater systems and to assess range management strategies to protect human and environmental health.

TREECS will be accessible from the World Wide Web and will initially have two tiers for assessments. Tier 1 (Dortch et al. 2009) consists of screening-level methods that require minimal data input requirements and can be easily and quickly applied by Army environmental staff to assess the potential for MC migration to surface water and/or groundwater MC with concentrations exceeding protective health benchmarks. Various simplifying assumptions, such as steady-state conditions and no system losses, such as degradation, are made to provide conservative or worst-case estimates with Tier 1. If a potential concern is indicated by a Tier 1 analysis, then there would be cause to proceed to Tier 2 to obtain a more definitive assessment.

Tier 2 assessment methods will require more detailed site data, and will require more knowledge and skill to apply. However, these methods can be applied by environmental staff who have a cursory understanding of multimedia fate and transport. The Tier 2 approach will allow time-varying analyses and system losses. Such analyses should provide more accurate predictions with generally lower concentrations due to mediating effects of transport phasing/dampening, natural attenuation, and degradation. Tier 2 should prove even more valuable than Tier 1 for range management assessments given the fact that it includes the time domain; thus allowing assessment of the effectiveness of range use rotation over time as a management option. Both Tiers 1 and 2 focus on contaminant stressors and human and ecological health end point metrics.

## Objective

The objective of this report is to describe the approach and formulations that will be used for Tier 2 of TREECS. The information provided in this report is sufficient to serve as design specifications for the development of models and software that will comprise Tier 2. The details of the soil model formulations provided herein can also serve as documentation for that model.

## Scope

The Army's Operational Range Assessment Program (ORAP) is being conducted in two phases: a Qualitative Assessment (Phase I) and a Quantitative Assessment (Phase II). The results of Phase I placed ranges into one of two categories: unlikely and inconclusive. A range categorized as "unlikely" requires no further action, and it is placed into a five-year review cycle. Ranges categorized as "inconclusive" will require a follow-up Phase II assessment.

The Army completed all ORAP Phase I assessments at the end of FY 09. Phase II assessments commenced in FY 10 after the completion of all Phase I assessments. Given this timetable and the more comprehensive needs and challenges of the Phase II assessments, ERDC, in consultation with the Army Environmental Command (AEC), concluded that the Tier 1 and Tier 2 tools of TREECS could help support needs within the Phase II ORAP. Additionally, these tools should help address range management issues, such as how to operate a range to avoid problems with off-site migration of MC.

In general, the Tier 1 and 2 tools of TREECS should provide the following information to address the needs of the Army:

1. Given range use, estimate the MC residue mass loading rate to the range as mass (M) per time (T), M/T.
2. Given the mass loading rate of MC, estimate the soil concentration on the range area of interest and the mass fluxes (M/T) off the range to other media (e.g., surface water and groundwater).
3. Given the mass fluxes to other media, estimate the media concentrations at points of interest off-range.
4. Given the media concentrations at points of interest off-range, determine if protective health benchmark concentrations are exceeded.

This information can help environmental specialists determine whether there is potential for a particular range to develop into a human health or environmental hazard. Furthermore, range use strategies could be adjusted or managed in an effort to promote range sustainment while satisfying protective health requirements. Having an estimate of concentration versus time in groundwater and surface water will provide additional information that could be used in the design of sampling and monitoring strategies.

Both Tiers 1 and 2 can address the above needs, but the approach to each is different. The primary difference between the two is that Tier 1 is time-invariant or steady-state, and Tier 2 is time-varying. Including time-varying conditions in the analysis substantially increases the level of accuracy in the forecasts at the cost of needing more data and knowledge.

## 2 Approach

The approach taken for Tier 2 is similar to Tier 1 in many aspects, especially with regard to spatial dimensionality. However, there are far fewer simplifying assumptions made for Tier 2, as compared with Tier 1, since time is included in the analysis approach. The conceptual site model and the assumptions that will be made for Tier 2 are summarized in this chapter. Descriptions of the models are provided later in the chapters describing each model.

### Conceptual Model Description

For land-based firing ranges, four media are considered when determining MC fate: soil, vadose zone, groundwater or aquifer, and surface water (including surface water sediments). Potential air concentrations of MC are a limited, short-duration, local issue and are not considered for range sustainment. A conceptual site model (CSM) for range-generated MC is shown in Figure 1. MC residue loading first enters the range soil. MC can move from soil to surface water via rainfall-extracted runoff and erosion and from soil to the vadose zone via infiltration or leaching. MC can then percolate through the vadose zone into a receiving aquifer. Aquifer and surface water concentrations of MC depend on the location of interest within the receiving water, relative to the point of MC influx. Receiving water concentrations can be computed and compared with benchmarks for compliance. There can also be pathways from groundwater to surface water and vice versa; however, only the pathway from groundwater to surface water is considered important in Tier 2. There can be a pathway for interflow from soil to surface water in some situations as well. Interflow is horizontal water movement, rather than vertical infiltration, within the soil or vadose zone. This feature will be included in Tier 2 and will be discussed in Chapter 8.

The main differences between the Tier 1 CSM (Dortch et al. 2009) and the Tier 2 CSM shown herein is that Tier 2 includes the vadose zone and a link from groundwater to surface water. The link from groundwater to surface water can also be added later to Tier 1. Also, Tier 2 includes system losses, including degradation and volatilization, and solid phase mass dissolving to non-solid phase mass, whereas Tier 1 does not.

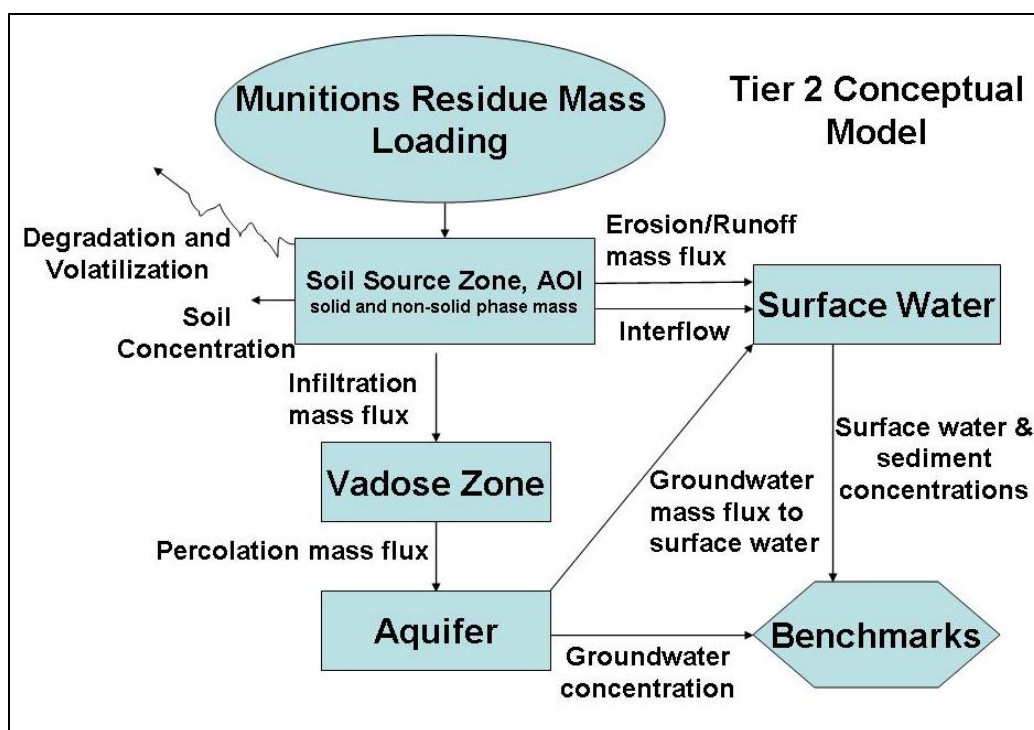


Figure 1. Tier 2 conceptual model schematic.

With the inclusion of time-varying conditions in Tier 2, it is necessary to include the vadose zone since mass transit time through the vadose zone can be quite long for some systems. There can also be mass loss within the vadose zone due to degradation.

The soil model will compute time-varying soil concentrations and mass export fluxes (M/T) for erosion, rainfall-extracted runoff, and infiltration. A portion of the infiltration flux can be designated as interflow with export to surface water rather than the vadose zone.

The vadose zone model will use the net infiltration, or leached mass influx rate, to compute the time-varying mass flux (M/T) entering the aquifer. The aquifer model will use the vadose zone mass flux and the receptor location to compute the time-varying groundwater concentration at the receptor location. Sorption and degradation can exist within the aquifer.

Mass flux imported by surface water can include soil compartment exports of runoff and erosion, plus interflow and groundwater discharge to surface water. The surface water models will use the time-varying mass influx imports to compute the time-varying surface water and sediment concentrations. There can be sorption, degradation, volatilization, mass



transfer between the water column and sediment bed, and sediment burial in the bed. The location of the receptor will not be required for one of the surface water models, but it is required for another surface water model that will be included for optional use. The latter surface water model computes concentration at the receptor location as described later. The models for each medium and their inputs and output are described later in this report.

The proof-of-concept testing of Tier 1 (Dortch et al. 2010) revealed that certain conditions needed to be imposed on the CSM and its implementation within TREECS. These conditions apply to Tier 1 and 2, and they include the following: each application will be for a single area of interest (AOI), and each AOI constitutes a separate application; each AOI will have no more than one aquifer and one surface water-body receiving loadings from the AOI being assessed.

When an impact area or AOI is within a single drainage basin, or sub-basin, of a watershed, designation of the AOI is relatively straightforward; the impact area should constitute a single AOI application. However, when an impact area is rather large and overlaps more than one sub-basin, it may be more accurate to split the impact area into multiple AOI. Such an example is shown in Figure 2 where the impact area overlaps two drainage basins. This example analysis could be conducted for two AOI, A and B. AOI A would use Lake A for the receiving water analysis, and AOI B would use Lake B. The difficulty with conducting an analysis like this is distributing the MC loadings between AOI A and B. Many firing ranges often fire into the same impact area. Range records usually denote the types and numbers of munitions fired from each range, but they do not describe where the projectiles hit. Thus, it is not possible to assign the AOI receiving the projectiles and their residue. One approach could be to distribute the residue loadings according to the fraction of total impact area that each AOI constitutes.

## **Basic Assumptions**

As with Tier 1, each AOI will be treated as a single fully mixed compartment; thus, soil concentrations are assumed to be uniform throughout the upper soil horizon within the AOI. As an example, the primary impact zone of a set of ranges will be treated as a single homogenous area. Although an AOI is, in fact, heterogeneous, treating a heterogeneous AOI as homogeneous is not a fatal assumption because the total MC source mass loading to soil is the

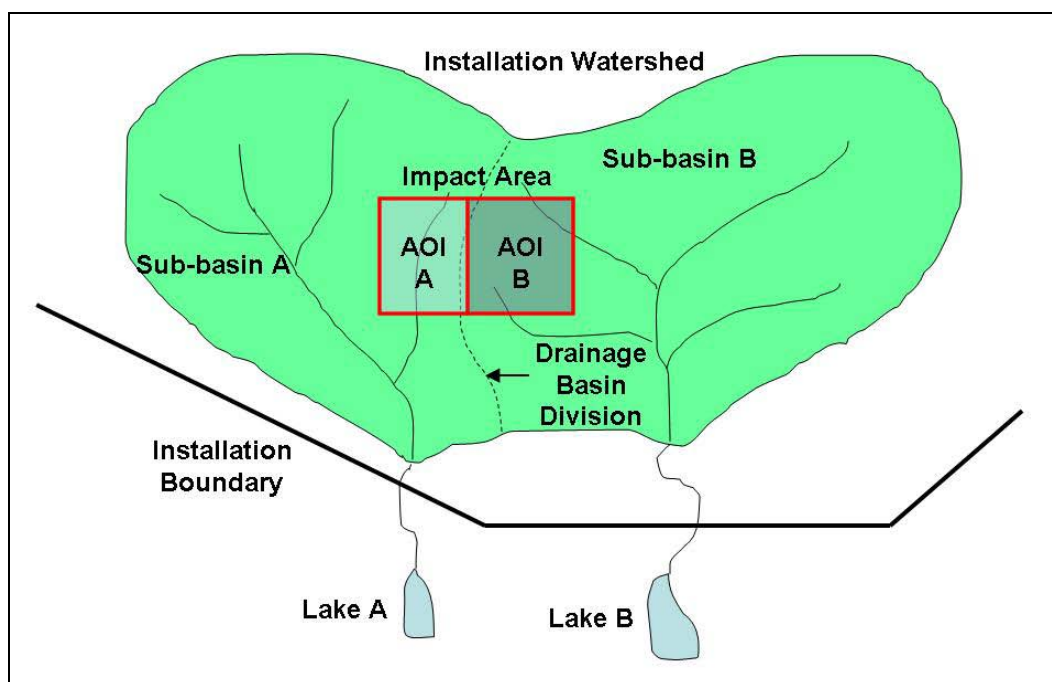


Figure 2. Example of an impact area that overlaps two drainage basins.

driving variable for export flux, not MC concentration in soil. Although the soil concentration of MC depends on heterogeneities and even the size of the source area for a homogeneous site, the fluxes or export rate of mass from the source area to other media does not depend on the area of the source zone or the source concentration. Of course, a large impact area with source mass clusters that differ substantially could be treated as multiple sources with each assessed individually. Predicted receiving media concentrations will be more conservative (i.e., higher concentrations) nonetheless if multiple source areas and the respective masses are combined.

The loading of MC into the AOI will be estimated from the numbers and types of munitions used on an annual basis. Additionally, the percentages for low order detonations, duds, and sympathetic detonations will be assigned for each type of munitions. Sympathetic detonations are duds that undergo a low order detonation due to a nearby high order detonation. The munitions yield, or percent of exploded energetic mass, must also be assumed and assigned for each munitions type and its associated detonation type. Initially, Tiers 1 and 2 of TREECS will address only impact areas and will not include firing points, but firing points could potentially be added later. Additionally, the user will have the option to specify a *known* loading rate of MC that may have been estimated.

Time-varying MC loadings and receiving media response can be assessed with Tier 2 since the steady-state assumption used for Tier 1 will not be made. Allowing for time-varying conditions increases model input requirements, but it also greatly increases the amount of output information available and can affect how receiving waters respond to range loadings and export. For example, if a loading of MC occurs for a ten-year period and then ceases, it may take another 10 years after the loading ceases for groundwater concentration to peak, and the arrival time and concentration level of the peak varies with the distance of the well from the source area and environmental factors. These variations can attenuate the groundwater concentrations to levels that can be substantially lower than would occur for continuous, long-term, steady-state MC loadings. Consequently, it is expected that receiving water concentrations will be generally lower for a Tier 2 analysis compared with a Tier 1 analysis.

The input requirements will be greater for Tier 2 than for Tier 1. System loss processes, such as degradation and volatilization, require input parameters. With a time-varying soil model, it will be possible to include corrosion/dissolution rates that drive the transformation of a solid phase MC mass to the more mobile aqueous phase. There are input parameters that will be required for dissolution processes. In addition, it will be necessary to input the initial soil concentration of MC when applying Tier 2. Tier 2 input requirements are discussed in greater detail later in this report.

The receiving surface water can be a stream, pond, lake, wetland, or any type of surface water. It will be assumed that any erosion mass trapped within the AOI drainage area prior to export from the AOI can be described with a sediment delivery ratio, or SDR, as discussed in Chapter 4. The use of the SDR is optional and will be calculated within the soil model and applied to eroded export fluxes computed by the soil model. It is assumed that there are no conveyance losses or trapping of MC mass between the AOI and receiving surface water-body for AOI exports to surface water; this provides a conservative, worst-case scenario while greatly reducing model complexity and data input requirements.

Transport through the vadose zone from soil to the groundwater will be treated as a one-dimensional (1D), vertical transport process. Lateral transport is not considered, and vertical transport is assumed to be uniform horizontally over the AOI. The aquifer transport is described as

unidirectional (1D), horizontal flow (advection) with three-dimensional (3D) dispersion along the flow axis. Degradation in the vadose zone and aquifer is assumed to be first order. Reversible, linear, equilibrium sorption is assumed in both media.

Two options will be provided for modeling MC fate in surface water. One option is the same model used in Tier 1 for surface water, which is the RECOVERY model. The second option is the Contaminant Model for Streams (CMS). The RECOVERY model treats the surface water column as a single, fully mixed compartment, which is zero-dimensional (0D). The water column is underlain with a 1D series of vertical layers with varying properties and concentrations. The CMS treats the surface water as a series of nodes where concentrations are uniform at a node (i.e., uniform over the depth and width of the water) but vary from node to node or along the length of the water body (i.e., in the longitudinal direction). Each node includes a benthic sediment compartment in addition to the water column, and there can be mass transferred between water and sediment; but no mass transfer is allowed between sediment compartments in adjacent nodes (i.e., 0D at a node). Sediment concentrations can also vary from node to node in the longitudinal direction. The RECOVERY model is best suited for standing or pooled water, such as pond and lakes. CMS is best suited for freely moving water, such as streams and rivers. Either model can be applied to any type of surface water body, but the user should understand the ramifications of the basic assumptions: i.e., 0D water column and 1D sediment representation in RECOVERY and 1D water column in CMS. The CMS is best suited for tidal streams as discussed in Chapter 6.

Like Tier 1, Tier 2 will use steady-state hydrologic inputs to compute model fate processes. The long-term average rates for annual soil erosion, rainfall and precipitation, and infiltration will be used for the soil model. Similarly, input rate parameters for fate processes are assumed to be constant over the simulation. The use of average annual hydrology and rate parameters does not preclude employing a time-varying contaminant fate model since the contaminant mass balance equations are time-varying. Time-varying concentrations and export fluxes will result even with constant input parameter. However, the time-varying results will approach steady-state if the MC loadings are constant in time. The use of constant input parameter greatly reduces model complexity and increases model ease-of-use.

The formulations or descriptions for the models used within Tier 2 of TREECS are described in Chapters 3 through 6. These models include: MC residue mass loading to soil, MC fate and export in soil, MC fate/transport in vadose zone, MC fate/transport in aquifer, and MC fate/transport in surface water and surface water sediment. Other modeling assumptions are addressed within each of these chapters.

### 3 MC Residue Mass Loading Model

The MC residue mass loading model for Tier 2 will be similar to the one for Tier 1; the primary difference is that munitions use can be varied on an annual basis rather than being constant over time. For each munitions item used, the user first selects the munitions identification using the munitions type and the Department of Defense identification code (DODIC) or National Stock Number (NSN). For each item, the user then provides the following for each year of input:

- The year that the item was used
- The number fired per year
- The percent of duds
- The percent of low order detonations
- The percent yield (portion of MC used up when munitions explode) for low order detonations
- The percent of duds that are sympathetically exploded by another detonation
- The percent yield for sympathetic detonations
- The percent yield for high order detonations.

TREECS will include help files for setting the above percentages. The percent of high order detonations is calculated from 100 percent minus the percentages of duds and low orders, and the calculated value is entered in the input table. The user cannot change this displayed value except for changing either the percentage of duds or low orders.

The item usage per year is stepped; i.e., the input numbers remain constant until the next update year in the input table. An example of the input screen for the Tier 2 MC residue mass loading model is shown in Figure 3. In this example, the usage for DODIC C445 is 500 firings per year from 1950 through 1954. In 1955, the firing of this item increased to 1000 per year. Notice that the other input parameters can also vary annually. If only one line of annual input is supplied within the munitions usage table for each munitions item, then the residue mass loading would be constant over time, or time-invariant, as in Tier 1 TREECS.

**TREECS - Training Range Environmental Evaluation and Characterization System**

File References Web Data Tools Websites Options Help

Installation/AOI Description Tier Analysis Selection Site Conditions DoD Target Health Benchmarks Inputs Execute Uncertainty View Results

Constituent Selection Operational Inputs

Type of loading to be estimated:  
☒ Impact Zone  
☐ Firing Point

Munitions master list:  
 CTG 81MM ILLUM M301 W/FUZE TIME M84 (NSN: 1315000284964) (DODIC: C226)  
 CTG 81MM ILLUM M301 W/FUZE TIME M84 (NSN: 1315001437122) (DODIC: C226)  
 CTG 81MM ILLUM M301 W/FUZE TIME M84 (NSN: 1315001645290) (DODIC: C226)  
 CTG 105MM HE M1 W/O FUZE (NSN: 1315000284809) (DODIC: C445)  
 CTG 105MM ILLUM M314A3 (NSN: 1315007825531) (DODIC: C449)

Search: Find/Find Next

Munitions used at this site/range:  
 CTG 105MM HE M1 W/O FUZE (NSN: 1315000284809) (DODIC: C445)

Munitions usage information:  
 Munition: CTG 105MM HE M1 W/O FUZE (NSN: 1315000284809) (DODIC: C445)  
 Starting year of simulation: 1950

	Time (yr)	Rounds Fired/yr	Dud (%)	Low Order (%)	Low Order Yield (%)	Sympathetic Duds (%)	Sympathetic Duds Yield (%)
▶	1950	500	1	2	50	1	75
	1955	1000	1.5	2.1	55	1.5	80

Note: All values are assumed constant between years. (If you have values only at years 0 and 100, then the values at time 0 apply for years 0-99 and the value at year 100 applies only at year 100 and then a value of 0 is assumed after that. If you have values only at years 10 and 50, then the values at time 10 apply for years 10-49 and output will start at year 10.)

Help

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 CTG 105MM ILLUM M314A3 (NSN: 1315007825531) (DODIC: C449)

Search: Find/Find Next

Munitions used at this site/range:  
 CTG 105MM HE M1 W/O FUZE (NSN: 1315000284809) (DODIC: C445)

Munitions usage information:  
 Munition: CTG 105MM HE M1 W/O FUZE (NSN: 1315000284809) (DODIC: C445)  
 Starting year of simulation: 1950

	Dud (%)	Low Order (%)	Low Order Yield (%)	Sympathetic Duds (%)	Sympathetic Duds Yield (%)	High Order (%)	High Order Yield (%)
▶		2	50	1	75	97	99.999
		2.1	55	1.5	80	96.4	99.997

Note: All values are assumed constant between years. (If you have values only at years 0 and 100, then the values at time 0 apply for years 0-99 and the value at year 100 applies only at year 100 and then a value of 0 is assumed after that. If you have values only at years 10 and 50, then the values at time 10 apply for years 10-49 and output will start at year 10.)

Help

Figure 3. Example of input screen for Tier 2 MC residue mass loading model.

In order to conduct the estimates of MC residue loading, it is necessary to first know the amount of MC mass in each munitions item that is delivered to the impact area. This information can be obtained from the Munitions Items Disposition Action System (MIDAS) (<https://midas.dac.army.mil/>) based on DODIC or NSN. However, extraction of information from MIDAS can be

slow and tedious. A utility has been developed for automatically pulling this information into the TREECS application using the DODIC or NSN. This utility requires a special, processed subset database of MIDAS that was developed by the Defense Ammunition Center, DAC. The MIDAS subset database presently includes data for 164 DODIC items, but this database can and should be expanded to include more items.

Once the MC mass delivered to the impact area is known for each munitions item used, the calculation of residue mass loadings is a straightforward summation. The MC residue mass loading for constituent  $i$  for year  $k$ ,  $L_{i,k}$ , (g/yr) is computed as follows,

$$L_{i,k} = \sum_{j=1}^{j=n} \left\{ N_{j,k} M_{i,j} \left[ \frac{LO_{j,k} (100 - Y_{LOj,k}) + HO_{j,k} (100 - Y_{HOj,k}) + DUD_{j,k} SYM_{j,k} (100 - Y_{SYMj,k})}{100} \right] \right\} \quad (1)$$

where

$DUD_{j,k}$  = percent of duds for munitions item  $j$  for year  $k$

$HO_{j,k}$  = percent of high order detonations for munitions item  $j$  for year  $k$

$LO_{j,k}$  = percent of low order detonations for munitions item  $j$  for year  $k$

$M_{i,j}$  = mass of constituent  $i$  in munitions item  $j$  delivered to impact area, g/item

$N_{j,k}$  = number of munitions item  $j$  fired for year  $k$

$n$  = total number of munitions items used at AOI

$SYM_{j,k}$  = percent of sympathetic detonation of duds for munitions item  $j$  for year  $k$

$Y_{HOj,k}$  = percent yield of munitions item  $j$  due to high order detonation for year  $k$

$Y_{LOj,k}$  = percent yield of munitions item  $j$  due to low order detonation for year  $k$

$Y_{SYMj,k}$  = percent yield of munitions item  $j$  due to sympathetic detonation for year  $k$

Thus, the number of items fired, the detonation type percentages, and the percent yields can vary on an annual basis. As stated previously, the percent of low order detonations, duds, and high order detonations must sum to 100 percent for each year of input. Additionally, annual input values must be provided for each munitions item designated as used at the AOI. There is



fairly good guidance on dud and low order rates (Concurrent Technologies Corporation 2004) for detonations, but there is only limited information on percent yield (Gerald et al. 2007). There is currently no guidance on percentage of sympathetic detonations. The residue mass loading model will also include the capability to specify a user-defined or known mass loading rate for each constituent rather than using the rates computed based on munitions usage.

## 4 Time-Varying Soil Model

Consider a compartment of surface soil of thickness or depth  $Z_b$  (m) over a given area of interest (AOI) with surface area  $A$  (m<sup>2</sup>). Assume that the MC concentration varies with time but is homogeneous or fully mixed throughout the soil compartment that is being loaded with solid phase MC residue. Thus, a continuously stirred tank reactor (CSTR) model is assumed for the soil model. The constituent is assumed to exist in solid (free product) and non-solid (dissolved from solid) phases. The non-solid phase mass exists in equilibrium distributed as dissolved in water within the water filled soil pore spaces, as adsorbed from water to soil particles, and as a vapor in air within the air filled pore spaces. A time-varying mass balance is performed for both the solid and non-solid phases.

### Solid Phase Mass Balance

The solid phase (free product without precipitation from aqueous phase) mass balance is stated as

$$\frac{dM_s}{dt} = L(t) - F_{dis} - F_{es} + F_{precip} \quad (2)$$

where  $M_s$  is the solid phase mass (g),  $t$  is time (yr),  $L(t)$  is time-varying solid phase MC mass loading (g/yr),  $F_{dis}$  is dissolution flux (g/yr),  $F_{es}$  is the erosion flux of solid phase particles (g/yr), and  $F_{precip}$  is the precipitation flux (g/yr), due to dissolved pore water concentration exceeding the water solubility limit. Loading depends on munitions use each year as described in Chapter 3. The dissolution and precipitation fluxes will be described later in this chapter, and the solid phase particle erosion flux is described in Appendix A.

### Non-Solid Phase Mass Balance

The non-solid phase mass balance is stated as

$$\frac{dM_{ns}}{dt} = F_{dis} - F_r - F_e - F_l - F_{decay} - F_{vol} - F_{precip} \quad (3)$$

where  $M_{ns}$  is non-solid phase mass (g),  $F_r$  is the rain-induced pore water ejection and runoff flux (g/yr),  $F_e$  is MC flux due to soil erosion (g/yr),  $F_l$  is leaching flux (g/yr),  $F_{decay}$  is degradation flux (g/yr), and  $F_{vol}$  is volatilization flux (g/yr). The total (particulate, dissolved, and vapor) non-solid phase constituent concentration within the soil matrix on a total volume basis,  $C_{tt}$  (g/m<sup>3</sup>) is

$$C_{tt} = \frac{M_{ns}}{V} = \frac{M_{ns}}{A Z_b} = \frac{M_d + M_p + M_a}{A Z_b} \quad (4)$$

where  $V$  is the surface soil compartment volume (m<sup>3</sup>) of the AOI. The terms  $M_d$ ,  $M_p$ , and  $M_a$  are the mass dissolved, mass adsorbed to soil particles, and mass of vapor in air (g), respectively. Note that the surficial soil layer thickness  $Z_b$  (m) and site area  $A$  (m<sup>2</sup>) are assumed to be constant in time. Thus, it is assumed that an active soil layer of the same thickness is reestablished, although there is soil loss due to erosion. The total non-solid concentration can be expressed as the sum of the three phase media concentrations corrected for media volumes or mass,

$$C_{tt} = \theta_w C_l + (\phi - \theta_w) C_g + \rho_b C_a \quad (5)$$

where

$C_l$  = concentration dissolved in pore water or liquid phase,  $M_d/V_w$ , g/m<sup>3</sup>

$C_g$  = vapor or gas concentration in air,  $M_a/V_a$ , g/m<sup>3</sup>

$C_a$  = concentration adsorbed to soil particles,  $M_p/M_{soil}$ , mg/kg

$\theta_w$  = soil volumetric moisture content or ratio of water volume to total volume, fraction;  $\theta_w$  can't be greater than soil porosity

$\phi$  = soil porosity or ratio of void volume to total volume, fraction

$\rho_b$  = soil dry bulk density, g/ml or kg/L

$V_w$  = volume of water in the AOI soil, m<sup>3</sup>

$V_a$  = volume of air in the AOI soil, m<sup>3</sup>

$M_{soil}$  = mass of soil in the AOI, g

The vapor and particulate concentrations can be related to the liquid concentration through phase equilibrium partitioning,

$$C_a = K_d C_l \quad (6)$$

$$C_g = K_H C_l \quad (7)$$

where  $K_d$  (L/kg) is the distribution coefficient for partitioning a constituent between soil particles and water, and  $K_H$  is the dimensionless Henry's constant for partitioning between air and water.  $K_H$  is computed from Henry's law constant  $H_e$  (atm $\theta$ m<sup>3</sup>/g-mol),

$$K_H = \frac{H_e}{R_u T_a} \quad (8)$$

where  $R_u$  is the universal gas constant = 8.206 E-5 atm $\theta$ m<sup>3</sup>/g-mol <sup>0</sup>K, and  $T_a$  is ambient absolute temperature (<sup>0</sup>K), or soil-water matrix temperature in this case, which is the temperature in <sup>0</sup>C plus 273. Substitution of Equations 6 and 7 into Equation 5 results in

$$C_l = \frac{C_{tt}}{\theta_w R} \quad (9)$$

where the retardation factor  $R$  is defined as

$$R = 1 + \frac{(\phi - \theta_w) K_H + \rho_b K_d}{\theta_w} \quad (10)$$

## Flux Terms

The discussions of flux terms are divided among those that are more easily described (leaching, degradation, volatilization, and soil erosion) and those that have a more involved description and derivation, which include rainfall-induced pore water extraction and runoff and dissolution. Thus, three flux term sections follow below. The solid phase constituent particle erosion flux is discussed in Appendix A, because the computation of this flux term requires special considerations and discussion.

### Leaching, Degradation, Volatilization, and Soil Erosion Fluxes

The leaching flux is computed from

$$F_l = q_w A C_l \quad (11)$$

where  $q_w$  is the average annual Darcy water infiltration rate (m/yr). Although the soil model is time-varying, annual average values are used for the hydrologic fluxes, which greatly simplify model input without compromising the long-term fate forecasts due to the linearity in flux process descriptors. Substitution of Equation 9 into Equation 11 results in

$$F_l = \frac{q_w A C_{tt}}{\theta_w R} \quad (12)$$

The degradation flux  $F_{decay}$  is computed from

$$F_{decay} = A Z_b (\lambda_l \theta_w C_l + \lambda_a \rho_b C_a) \quad (13)$$

where  $\lambda_l$  and  $\lambda_a$  are the degradation rates ( $\text{yr}^{-1}$ ) for the liquid (aqueous dissolved) and aqueous adsorbed concentrations, respectively. It is assumed that the vapor phase does not degrade, but it can volatilize-- or diffuse -- from the soil into the overlying air. Using Equations 6 and 9, Equation 13 can be rewritten as

$$F_{decay} = A Z_b \left( \lambda_l \frac{C_{tt}}{R} + \lambda_a \rho_b K_d \frac{C_{tt}}{\theta_w R} \right) \quad (14)$$

The volatilization flux  $F_{vol}$  is computed from

$$F_{vol} = K_v A (\phi - \theta_w) C_g \quad (15)$$

where  $K_v$  is the volatilization rate (m/yr), or vapor escape rate from soil to the overlying air. The calculation for  $K_v$  is discussed later below in a separate section following the Flux Terms section. Using Equations 7 and 9, Equation 15 can be rewritten as

$$F_{vol} = K_v A (\phi - \theta_w) K_H \frac{C_{tt}}{\theta_w R} \quad (16)$$

Equations 12, 14, and 16 can be rewritten as follows

$$F_l = \frac{q_w}{\theta_w} A F_{dp} C_{tt} \quad (17)$$

$$F_{decay} = A Z_b (\lambda_l F_{dp} C_{tt} + \lambda_a F_{pp} C_{tt}) \quad (18)$$

$$F_{vol} = K_v A F_{ap} C_{tt} \quad (19)$$

The quantity  $\frac{q_w}{\theta_w}$  is the pore water infiltration rate. The factors  $F_{dp}$ ,  $F_{pp}$ , and  $F_{ap}$  are used to convert from total concentration on a total volume basis to dissolved, particulate, and air concentrations, respectively, in the porous media on a total volume basis. These factors are defined as

$$F_{dp} = \frac{\theta_w}{\theta_w + (\phi - \theta_w) K_H + \rho_b K_d} = \frac{1}{R} \quad (20)$$

$$F_{pp} = \frac{\rho_b K_d}{\theta_w + (\phi - \theta_w) K_H + \rho_b K_d} \quad (21)$$

$$F_{ap} = \frac{(\phi - \theta_w) K_H}{\theta_w + (\phi - \theta_w) K_H + \rho_b K_d} \quad (22)$$

It is pointed out that the formulation for  $F_{dp}$  here is different from the one used in the steady-state soil model (Dortch et al. 2009).

The erosion flux is computed from

$$F_e = E A C_{tt} \quad (23)$$

where  $E$  is the average annual soil erosion rate (m/yr). It can be shown that  $F_e$  includes the flux of chemical adsorbed to eroded soil particles and pore water chemical that is within the eroded soil layer.

### Rainfall-Induced Pore Water Ejection and Runoff Flux

Rain-induced pore water ejection and runoff is used to estimate runoff flux  $F_r$ . Chemicals can be transferred from soil pore water to overland runoff due to rainfall impacting the soil surface, even when there is no erosion. The event-based runoff mass removal rate of pore water  $Re_{dQ}$  (g/sec) due to rain-induced ejection can be computed (Gao et al. 2004) from

$$Re_{dQ} = e_r A \bar{C}_e \quad (24)$$

where  $e_r$  (m/sec) is the rate of soil pore water ejection during a rainfall event, and  $\bar{C}_e$  is the rainfall event's time-averaged soil pore water chemical concentration (g/m<sup>3</sup>) in the soil exchange layer adjacent to the overland water. The soil water ejection rate  $e_r$  is defined (Gao et al. 2004) as

$$e_r = \frac{aI\phi}{\rho_b} \quad (25)$$

where  $I$  is the rainfall intensity (m/sec),  $a$  is the soil detachability (kg/L), and  $\phi$  is the saturated water content, which is the soil porosity. The instantaneous soil pore water chemical concentration in the exchange layer during a rainfall event can be approximated (Gao et al. 2004) by

$$C_e \approx C_o \exp(-\beta t) \quad (26)$$

where  $C_o$  is the soil pore water concentration below the exchange layer and is equal to  $F_{dp}C_{tt}/\theta_w$  or  $C_l$ ,  $t$  is time (sec), and

$$\beta = \frac{e_r F_{dp}}{d_e \theta_w} \quad (27)$$

where  $d_e$  is the soil exchange layer thickness (m);  $\beta$  has units of sec<sup>-1</sup>. The event time average of Equation 26 is

$$\bar{C}_e = \frac{C_o \int_0^T e^{-\beta t} dt}{T} = \frac{C_o}{T\beta} (1 - e^{-\beta T}) \quad (28)$$

where  $T$  is the time averaging interval, which is the event duration (sec). Substituting the definition of  $C_o$  and Equations 25, 27, and 28 into Equation 24 results in

$$\text{Re}_{dQ} = \frac{Ad_e}{T} (1 - e^{-\beta T}) C_{tt} \quad (29)$$

The goal is to be able to apply Equation 29 to develop an average annual rainfall extraction of pore water with runoff. To do this, an average or typical rainfall intensity  $\bar{I}$  and associated duration  $\bar{T}$  are required for use in Equations 25, 27, and 29, resulting in an average event runoff flux,

$\overline{\text{Re}_{dQ}}$ . Multiplying  $\overline{\text{Re}_{dQ}}$  by  $\bar{T}$  results in the average event pore water mass removed with runoff. The number of such events occurring within a year,  $N$  (events/yr), can be multiplied times  $\overline{\text{Re}_{dQ}}\bar{T}$  to obtain the pore water mass removed with runoff per year or the annual runoff export  $F_r$ . The above statements are expressed in mathematical form as

$$F_r = Ad_e \left(1 - e^{-\bar{\beta}\bar{T}}\right) C_{tt} N \quad (30)$$

The values used for  $\bar{I}$ ,  $\bar{T}$ , and  $N$  should satisfy the following relation,

$$P_r = \bar{I} \bar{T} N \quad (31)$$

where  $P_r$  is the average annual rainfall (m/yr), not total precipitation.  $\bar{T}$  and  $\bar{I}$  drop out of Equation 30 when  $\bar{\beta}$  is multiplied by  $\bar{T}$  since  $\bar{\beta}$  has rainfall intensity in it, which is a function of  $\bar{T}$ ,  $P_r$ , and  $N$  (see Equation 31). Thus, the average event intensity and duration do not affect the annual export; rather it is the annual rainfall and number of rainfall events that are important for computing annual rainfall extracted pore water runoff export. A reasonable approach is to count the number of days per year that rainfall occurs to approximate  $N$ . Equation 30 can be rewritten as shown below given the above discussion,

$$F_r = Ad_e \left(1 - e^{-\kappa}\right) C_{tt} N \quad (32)$$

where,

$$\kappa = \frac{a\phi F_{dp} P_r}{\rho_b \theta_w d_e N} \quad (33)$$

During rainfall events, the upper soil is water-saturated, and  $\theta_w$  equals  $\phi$ , which affects the calculation of  $F_{dp}$  and  $\kappa$ . Thus, Equation 33 becomes,

$$\kappa = \frac{aP_r}{\rho_b d_e N} \left( \frac{\phi}{\phi + \rho_b K_d} \right) \quad (34)$$

The result computed by Equations 32 and 34 is fairly sensitive to all input parameters. However, the only two parameters that are not easily determined are  $d_e$  and  $a$ , so typical values found in the literature like those



reported by Gao et al. (2004) must be used. It is expected that both of these parameters are affected by soil texture, land use and cover, and possibly soil chemistry. It is emphasized that  $P_r$  in Equation 34 is rainfall rather than total precipitation; thus, snow is not included, and  $N$  is the number of rainfall days, not the number of precipitation days.

### Dissolution Flux

The objective was to develop a general dissolution formulation that provides estimates of solid phase mass transferred to the aqueous phase on an annual basis using average annual input conditions so that long-term (decadal) forecasts can be easily conducted. The formulation needed to take into account dissolution for the total solid phase mass deposited within the AOI, not merely an individual particle, and should be applicable to various types of solid phase MC, such as metals and HE.

Dissolution of a solid particle in water can be described as a diffusion process (Cussler 1997) driven by the concentration gradient around a solid particle, which is expressed as

$$\frac{dm_i}{dt} = -\frac{D_w}{h} A_{si} (C_s - C_{la}) \quad (35)$$

where

$m_i$  = solid phase mass for particle  $i$ , g

$D_w$  = chemical's aqueous phase diffusion coefficient, cm<sup>2</sup>/sec

$A_{si}$  = surface area of the individual solid phase particle, cm<sup>2</sup>

$C_s$  = aqueous solubility of the chemical, g/cm<sup>3</sup>

$C_{la}$  = chemical concentration in water adjacent to the particle, g/cm<sup>3</sup>

$h$  = the boundary layer film thickness around the particle, cm

$t$  = time, sec

During quiescent conditions of no water movement, such as with no rainfall,  $C_{la}$  approaches  $C_s$ , and there is no dissolution. Thus, it can be assumed that dissolution occurs only when water is moving past the particles as when it is raining, which is the case with the drop impingent model developed by Taylor et al. (2009a). If water is continually replaced around the particle when it is raining such that the adjacent water concentration is dilute,  $C_{la}$  can be assumed to be much smaller than  $C_s$ . Equation 35 simplifies to

$$\frac{dm_i}{dt} = -\zeta C_s A_{si} \quad (36)$$

where  $D_w/h$  has been parameterized with  $\zeta$ , the dissolution mass transfer rate or solid phase surface removal rate (cm/sec). The product of  $\zeta$  and  $C_s$  is the mass dissolution flux rate  $\beta_m$  (g/cm<sup>2</sup>-sec). The mass dissolution flux rate  $\beta_m$  lumps various processes to account for weathering, corrosion, and dissolution and depends on constituent solubility, which for metals can depend on a number of site-specific conditions, such as soil redox potential, pH, soil chemistry, and other factors.

The change in total solid phase mass  $m$  over time (g/sec) for all particles is

$$\frac{dm}{dt} = -\zeta C_s \alpha m = -\beta_m \alpha m = -F_{dis} \quad (37)$$

where  $\alpha$  is the average specific surface area (cm<sup>2</sup>/g) of the solid phase mass and depends on the distribution of the size and shape of the solid phase particles and the constituent solid phase density. The product  $\alpha m$  is the total surface area of solid phase particles. The total solid phase mass  $m$  is the same as the previously defined variable  $M_s$ . The value of  $\alpha$  generally increases as the particles dissolve and total mass decreases.

Previously reported dissolution models for high explosives, such as those reported by Phelan et al (2004), Taylor et al. (2009a), and Lynch et al. (2002), can be recast in a form similar to Equation 37. The Phelan model is similar to Equation 35 with the mass transfer rate  $D_w/h$  determined from soil column leaching studies.

The Lynch model is

$$\frac{dm}{dt} = -\alpha m \beta_m e^{\theta T_w} \quad (38)$$

where  $T_w$  is ambient water temperature in degrees C, and  $\theta$  here is an empirical coefficient to account for temperature effects on dissolution rate due to changes in solubility. Equation 38 is already in the same form as Equation 37. The values of  $\theta$  and the mass dissolution flux rate  $\beta_m$  depend on the explosive constituent and were determined experimentally from batch-mixing studies. Values of  $\theta$  were found to vary between 0.0574 and

0.0903 per °C, and  $\beta_m$  was found to vary between 1E-6 and 7E-5 mg/cm<sup>2</sup>-sec. The Lynch model tends to produce rapid dissolution rates since the fitted  $\beta_m$  parameter was developed from continuous batch-mixing studies.

The Taylor-Lever model (Lever et al. 2005 and Taylor et al. 2009a) is based on individual impingent rain drops and for small particles is stated as

$$\frac{dm}{dt} = -C_s \frac{V_l}{t_d} \quad (39)$$

where  $V_l$  is water layer volume (cm<sup>3</sup>) coating a spherical explosive particle and is a function of the water thickness  $h$  coating the particle;  $t_d$  is the rain drop arrival interval (sec). This model is valid for  $t_d > h^2/D_w$ , which is satisfied for the experimental results. Values for  $h$  were determined by fitting laboratory experimental results from water dropping on individual particles, and the value was found to be on the order of 0.1 mm (Taylor et al. 2009b).

For a thin water layer  $h$  and relatively large solid particles (e.g., on the order of 1 mm or greater),  $V_l$  can be approximated as the product  $A_{si}h$  for an individual particle, and the ratio  $h/t_d$  is similar to a surface renewal (or removal) rate,  $\zeta$ . Thus, Equation 39 can be recast in the form of Equation 36 and Equation 37.

Equation 37 is used as the basis for the dissolution formulation within the TREECS Tier 2 soil model, except that it is cast in a form that can be used to estimate annual rates. Consider precipitation rate as the driving force for the mass transfer or water removal rate,  $\zeta$ . Recent results of Taylor et al. (2009b) indicate that there is a linear relationship between dissolution rate and precipitation rate, and they demonstrate that it is possible to link annual HE dissolution flux to annual precipitation. Thus, Equation 37 can be recast by replacing  $\zeta$  with average annual total precipitation  $P_t$  (cm/yr or m/yr depending on the units of  $\alpha$  and  $C_s$ ) resulting in

$$F_{dis} = P_t \alpha M_s C_s \quad (40)$$

Taylor et al. (2009b) included snowfall in equivalent rainfall amount in their calculations for comparison with experimental results. Thus, total precipitation is used in Equation 40. Appendix B presents the application and comparison of Equation 40 to experimental data of Taylor et al.

(2009b) and comparison with results of the linear, annualized, Taylor-Lever model (Taylor et al. 2009b). The results from Equation 40 compare favorably with both experimental results and the linear Lever-Taylor model as discussed in Appendix B.

All other variables in Equation 40 have been previously defined. However, relationships are required for estimating  $\alpha$  and  $C_s$ . Considering two solid particle shapes, spherical and cylindrical,  $\alpha$  can be derived for each shape as a function of particle average diameter  $d_i$  (cm) resulting in

$$\alpha(\text{cylinder}) = \frac{2}{\rho_{sm} l} + \frac{4}{\rho_{sm} d_i} \quad (41)$$

$$\alpha(\text{sphere}) = \frac{6}{\rho_{sm} d_i} \quad (42)$$

where  $\rho_{sm}$  is the solid phase constituent mass density (g/cm<sup>3</sup>), and  $l$  is the length (cm) of a right cylinder. The particle diameter  $d_i$  and the specific surface area  $\alpha$  vary with time as mass is dissolved from the particles. For a constant particle density, it can be shown (Phelan et al. 2002) that average particle diameter  $d_i$  can be related to total particle mass  $M_s$ , which varies over time, with the result

$$d_i(t) = d_i(t - \Delta t) \left\{ \frac{M_s(t)}{M_s(t - \Delta t)} \right\}^{1/x} \quad (43)$$

where  $t$  is time, and  $\Delta t$  is the time step in the solution procedure. Since  $M_s$  is being calculated each time step,  $d_i$  and thus  $\alpha$  can be computed each time step. The value of  $x$  in the exponent of Equation 43 is 3 for spherical particles and 2 for cylindrical particles of constant length  $l$ . If solid phase mass is decreasing with time, the average particle diameter decreases with time and vice versa. However, the average particle diameter at the new time step is not allowed to exceed the initial average particle diameter. Thus, if MC mass is continually being loaded into the AOI at a rate such that solid phase mass is continually increasing, then the average particle diameter will be held constant at the initial value. Also, the average particle diameter should not be allowed to decrease below a minimum particle diameter (such as 1.0 E-9 m) to avoid division by zero in Equation 42. In reality, older particles are shrinking and are smaller than more recently loaded and

newer particles. The only way to improve upon the present simplification would be to track the fate of the individual MC mass classes deposited in the AOI each year. This could be a model refinement for future consideration.

The primary reason for included two particle shapes is to investigate the effect of shape on results. Usually, the preferred choice would be spherically shaped particles. There is no guidance for using one shape over the other.

For organic MC, the water solubility  $C_s$  is a chemical property that varies with ambient water temperature. Phelan et al. (2002) measured  $C_s$  for the explosives RDX and TNT for varying temperature and came up with the relationships

$$C_s(TNT) = 20.176 + 36.295e^{\frac{T_w}{22.061}} \quad (44)$$

$$C_s(RDX) = \frac{1}{0.0804 - 0.0194 \ln T_w} \quad (45)$$

where  $T_w$  is water temperature (deg C), or soil-water matrix temperature in this case, and  $C_s$  has units of mg/L. The statistical  $r^2$  values for Equation 44 and 45 are 0.994 and 0.997, respectively.

Since Equation 40 is applied for annual inputs to produce annual fluxes, the value of  $C_s$  should be an annual average value. A reasonable and simplifying assumption is that soil water temperature from precipitation is approximately equal to air temperature. In fact, mean annual soil temperature in temperate, humid, continental climates can be approximated by adding 1 °C to the mean annual air temperature reported by standard meteorological stations (NRCS 1993). Thus, average annual air temperature is needed to compute solubility. Daily average air temperatures can be averaged over each year and over all the years for the period of record to obtain average annual air temperature.

Water solubility values exist for many organic chemical constituents for a standard temperature, such as 20 or 25 °C. However, water solubility of metals is much more variable and complex and depends on the soil-water mineral speciation and chemistry, including pH, total dissolved solids, alkalinity, and potentially other factors. Estimating solubility for metals is

beyond the scope of this report, but it does need to be addressed within the TREECS project and is addressed in a follow-on report pertaining to the Tier 2 proof-of-concept application (Dortch et al. 2011).

## Volatilization Rate

Volatilization from soil has been modeled by Jury et al. (1983) and others. Their one dimensional (vertical) soil models display contaminant concentrations that vary over soil depth as a result of diffusion within the soil, volatilization across the soil-air interface, and other processes, such as leaching and degradation. A simpler approach is needed here since the soil is treated as a single homogeneous layer, which precludes computing time-varying concentrations that vary with soil depth. However, implementing a simpler approach is difficult since volatilization mass transfer rate varies with time as contaminant mass is depleted near the soil surface due to volatilization.

The volatilization mass transfer rate  $K_v$  (m/yr) is required to compute the volatilization flux as shown in Equation 19. The volatilization rate is a transport coefficient across the soil-air boundary that can be approximated as a diffusion coefficient of the vapor divided by the diffusion length or thickness for mass transfer. It is assumed that the diffusion coefficient of the vapor in air above the soil surface is much greater than the diffusion coefficient of the vapor within the soil matrix due to the porosity and tortuous pathways between solid particles in the soil. Thus, diffusion within the soil layer is the limiting factor for volatilization. The effective diffusion rate coefficient for a vapor within air spaces of the soil matrix can be estimated from (Millington and Quirk 1961),

$$D_{G_{eff}} = D_G^{air} \frac{(\phi - \theta_w)^{10/3}}{\phi^2} \quad (46)$$

where  $D_{G_{eff}}$  is the effective diffusion coefficient (m<sup>2</sup>/day) for a vapor in soil, and  $D_G^{air}$  (m<sup>2</sup>/day) is the constituent vapor or gas diffusion coefficient in air.

Values for  $D_G^{air}$  are available for many of the constituents in the constituent databases that will be made available within TREECS. If values are not available within a database, then  $D_G^{air}$  for the constituent of interest at 20 deg C can be estimated (Lyman et al. 1982) from

$$D_G^{air} = 8.64 D_2 \sqrt{\frac{M_2}{M_1}} \quad (47)$$

where  $D_2 = 0.102 \text{ cm}^2/\text{sec}$ , which is the known diffusion coefficient for carbon disulfide in air;  $M_2 = 76 \text{ g/mole}$ , which is the molecular weight of carbon disulfide; and  $M_1$  is the molecular weight MW of the constituent of interest.

The volatilization rate is then,

$$K_v = 365 \frac{D_{G_{eff}}}{d_v} \quad (48)$$

where  $d_v$  is the diffusion layer thickness (m) in the top of the soil layer. This is different from the boundary layer thickness immediately above the soil-air interface, which is much smaller and can vary with wind speed and other factors. The air boundary layer thickness has a value on the order of 1 mm (0.001 m) as calculated from experimental data (Spencer et al. 1988 and Hanna et al. 1982). With the lower effective diffusion coefficient and the larger diffusion thickness, it is easy to see why volatilization mass transfer rate in soil is the limiting factor, and the mass transfer rate above the soil-air interface is relatively unimportant when dealing with a single layer for the soil model. Additionally, the present model does not consider vertical migration of liquid phase constituent due to evaporation, which can also affect the volatilization flux (Jury et al. 1983).

The present model, including Equations 19, 22, 46-48, and the complete mass balance equations were applied for several chemicals which had volatilization fluxes reported in the literature that were computed with the Jury model (Jury et al. 1983) or a similar model of that type. The Jury model is considered a standard for determining volatilization from soil. By comparing results of the present model against reported flux rates, it was possible to determine an appropriate value for the diffusion thickness in soil  $d_v$ . These comparisons indicated that a value of about 0.4 m provided reasonable estimates. These comparisons are discussed below.

During the development of the CALTOX model ([http://www.dtsc.ca.gov/Assessing-Risk/ctox\\_dwn.cfm](http://www.dtsc.ca.gov/Assessing-Risk/ctox_dwn.cfm)), the Jury model was applied for trichloroethylene (TCE) and hexachlorobenzene (HCB) to aid in the development of a simpler

volatilization routine for CALTOX. The application and the results are described within the CALTOX documentation report (Office of Scientific Affairs 1993; ([http://www.dtsc.ca.gov/AssessingRisk/ctox\\_dwn.cfm](http://www.dtsc.ca.gov/AssessingRisk/ctox_dwn.cfm))). Given the initial soil concentration of  $100 \mu\text{mol}/\text{cm}^3$  uniformly distributed throughout the soil of depth 10 m, the Jury model indicated that the volatilization flux from the soil varied from approximately 60 and  $0.3 \mu\text{mol}/\text{cm}^2\text{-day}$  at year zero to approximately 0.5 and  $0.02 \mu\text{mol}/\text{cm}^2\text{-day}$  at year 10 for TCE and HCB, respectively. The model described above (with  $d_v = 0.4$  m for both chemicals) gave fluxes of 86 and  $0.026 \mu\text{mol}/\text{cm}^2\text{-day}$  at year zero and 3.9 and  $0.026 \mu\text{mol}/\text{cm}^2\text{-day}$  at year 10 for TCE and HCB, respectively. Although the present model does not give exactly the same result as the Jury model results, it does give approximately the same order of magnitude, which is encouraging given the simplicity of this model. The soil conditions used for the Jury model were not reported; therefore, they were assumed to be the following for the present model application:  $\rho_b = 1.48 \text{ kg/L}$ ;  $\phi = 0.44$ ;  $\theta_w = 0.175$ ; and fraction by weight of soil organic carbon,  $f_{oc} = 0.01$ . The chemical properties used for TCE and HCB, respectively, were:  $H_e = 9.69 \text{ E-3}$  and  $1.67 \text{ E-4 atm-m}^3/\text{gmole}$ ; molecular weight = 131.4 and 284.8; organic carbon – water partition coefficient,  $K_{oc} = 67.7$  and  $3380 \text{ L/kg}$ ; and zero degradation rates. The comparisons may have been closer if the soil conditions used for the Jury model had been known.

Jury et al (1990) present Jury model volatilization results for various chemicals in soil with and without a clean soil overburden. Results for benzene in sandy soil with no overburden (zero soil cover) after 1,000 days were used to compare with the present model. The soil conditions for the Jury model application were:  $\rho_b = 1.59 \text{ kg/L}$ ;  $\phi = 0.4$ ;  $\theta_w = 0.18$ ; and  $f_{oc} = 0.0075$ . The chemical properties used for benzene in the Jury model were:  $H_e = 5.29\text{E-3 atm-m}^3/\text{gmole}$ ; molecular weight = 78.1;  $K_{oc} = 80 \text{ L/kg}$ ; and degradation half life of 365 days. The soil layer thickness without cover and contaminated with benzene was 1.0 m. Again, the value used for  $d_v$  in the present model was 0.4 m. The present model projected that 91 percent of the benzene initial mass was volatilized after 1,000 days. This result compares closely with the approximately 89 percent reported by Jury et al. (1990).

Phelan and Webb (1997) applied the Jury model to validate a model they developed of similar design for buried mine detection. Thus, the Phelan model is a Jury type of model. They applied their model for TNT to evaluate how long it would take for TNT volatilization flux to be emitted at the soil



surface and the level of concentrations to expect over time. The present model was compared with surface flux computed from the Phelan model after the surface flux had reached nearly steady-state for a constant source loading from a buried mine. Results are compared for scenario 1 of the Phelan model study, which was for the mid-continent conditions. The soil conditions for the Phelan model application were:  $\rho_b = 1.5 \text{ kg/L}$ ;  $\phi = 0.44$ ;  $\theta_w = 0.25$ ; and  $f_{oc}$  was not specified since the  $K_d$  was specified. The chemical properties used for TNT in the Phelan model were:  $H_e = 1.44\text{E-}8 \text{ atm-m}^3/\text{g-mole}$ ; molecular weight = 222;  $K_d = 6.8 \text{ L/kg}$ ; and degradation half life of 180 days. For the Phelan model, the mine was located between a soil depth of 5 and 15 cm. The soil layer thickness contaminated with TNT for the present model was set to 0.15 m. A constant TNT source in the soil was input in the Phelan model at a soil depth of 10 cm at a rate of  $8.6\text{E-}6 \text{ }\mu\text{g/cm}^2\text{-day}$ . This same source load was input to the single 15-cm-thick layer of the present model. Again, the value of  $d_v$  used in the present model was 0.4 m. The fact that the soil layer thickness is less than  $d_v$  did not impede application of the present model.

The nearly steady-state surface volatilization flux after one year computed by the Phelan model was about  $1.0\text{E-}11 \text{ }\mu\text{g/cm}^2\text{-day}$ . The nearly steady-state flux computed by the present model was  $1.4\text{E-}10 \text{ }\mu\text{g/cm}^2\text{-day}$ . The present model is nearly steady-state from the beginning of the simulation since there is no layer of clean soil above the contaminated soil like there was in the Phelan modeling. The Phelan model results had not quite reached steady-state after one year and were still increasing slowly. Also, the Phelan model includes the effects of rainfall-evaporation cycles on migration in the soil, whereas the present volatilization model ignores the effects of evaporation on volatilization. The present model agrees with the Phelan model flux results within an order of magnitude, which is not bad considering the simplicity of the present model.

It is noted that a two film (or dual boundary) model was considered, where both the air side and the soil side boundary layer thicknesses and diffusion coefficients were considered like resistors in series. However, including the air side boundary had only a very minor effect on the results given the greater resistance associated the much smaller diffusion coefficient and much larger diffusion layer thickness on the soil side.

The relatively simple volatilization model proposed above provides reasonable orders of magnitude for volatilization flux for a wide range of

chemicals with widely ranging Henry's constants and for the same diffusion layer thickness of 0.4 m. Overall, the fluxes estimated with the proposed model are a little greater than those reported in the literature. However, volatilization will be a minor process relative to other loss pathways for MC since the Henry's constants are fairly small for most MC of primary interest, such as HE. The user has the option in TREECS to turn off the volatilization pathway by re-setting the estimated volatilization rate  $K_v$  to zero.

The soil layer thickness  $Z_b$  will be one of the inputs for the time-varying soil model of TREECS Tier 2. The soil contamination thickness can vary widely; therefore, this input can be uncertain. The sensitivity of this input variable on model results will need to be investigated during model testing, but initial testing indicates that it does slightly affect export fluxes. A value of about 0.5 m for  $Z_b$ , or even 0.4 m like  $d_v$ , seems reasonable. The value of  $Z_b$  will be an input provided by the user. If a value of  $Z_b$  is used that is less than the suggested value of  $d_v$  (i.e., 0.4 m), the model will still run without problems. The values used for  $d_v$  and  $Z_b$  are completely independent. The soil model user interface will allow the user to change the value of  $d_v$  from the default value of 0.4 m if desired for computing  $K_v$ .

## Equation Summary

### Without Solubility Limits

The above defined flux terms can be used to solve the non-solid phase mass balance (Equation 3) in terms of the unknown  $C_{tt}$ ,

$$AZ_b \frac{dC_{tt}}{dt} = F_{dis} - Ad_e(1 - e^{-\kappa})NC_{tt} - EAC_{tt} - \frac{q_w}{\theta_w}AF_{dp}C_{tt} - AZ_b(\lambda_l F_{dp} + \lambda_a F_{pp})C_{tt} - K_v AF_{ap}C_{tt} - F_{precip} \quad (49)$$

Collecting and cancelling terms in the above equation results in

$$\frac{dC_{tt}}{dt} = \frac{F_{dis}}{AZ_b} - \left[ \frac{d_e}{Z_b}(1 - e^{-\kappa})N + \frac{E}{Z_b} + \frac{q_w}{\theta_w Z_b}F_{dp} + (\lambda_l F_{dp} + \lambda_a F_{pp}) + \frac{K_v}{Z_b}F_{ap} \right] C_{tt} - \frac{F_{precip}}{AZ_b} \quad (50)$$

Equation 50 and Equation 2 constitute a system of two coupled ordinary differential equations that can be solved for the two unknowns,  $C_{tt}$  and  $M_s$ , which vary over time. The coupling terms are the dissolution and precipitation fluxes. The precipitation flux term in Equations 2 and 50 is zero when solubility is not limiting. After solving the concentration  $C_{tt}$ , all of the various flux terms defined above can be calculated for each time point and output as a time series for use as input loads to other models, such as leaching flux used by the vadose zone model.

### Including Solubility Limits

A check is required at the end of each time step update to see if the computed value of the soil pore water concentration  $C_l$  exceeds the solubility of the constituent in water  $C_s$  (g/m<sup>3</sup> or mg/L). If the value of  $C_l$  computed from Equation 9 exceeds  $C_s$ , then the precipitation flux  $F_{precip}$  is computed from

$$F_{precip} = \frac{AZ_b(C_l - C_s)}{\Delta t} \quad (51)$$

where  $\Delta t$  is the time step for the most recent time update of the solution. If  $C_l$  is less than  $C_s$ , then  $F_{precip}$  is zero for the next time step update.

If pore water MC concentration  $C_l$  exceeds solubility, then precipitation flux computed with Equation 51 is used in Equations 2 and 50 for the solution at the next time step.

The two differential equations (Equations 2 and 50) should be solved using the fourth-order-accurate Runge-Kutta time integration method with an option to use either a constant or variable time step that is automatically computed to maintain stability. Due to the variable time step option, it is recommended that the solution to equation 51 be lagged with the solution of Equations 2 and 50 as described above rather than trying to iterate the solution with those two equations, which could lead to convergence problems.

## 5 Vadose Zone and Aquifer Models

The groundwater below the AOI soil layer will be simulated with two models, an unsaturated (partially saturated) zone, or vadose zone model, and a saturated zone, or aquifer model. As constituent mass leaches from the upper soil horizon, it enters deeper soil layers that are partially saturated with water, and the only processes are vertical percolation, adsorption, and degradation. After passing through the vadose zone, the constituent mass reaches the top of the groundwater table and is then transported horizontally with the groundwater flow. A schematic for the groundwater transport modeling is shown in Figure 4.

The Multimedia Environmental Pollutant Assessment System (MEPAS) (Buck et al. 1995) consists of various models of reduced form for computing multimedia fate and transport, human exposure concentrations, and human receptor doses and health risks. The MEPAS groundwater models consist of time-varying contaminant fate/transport models of the vadose zone and aquifer. The MEPAS version 5.0 groundwater models (Whelan and Castleton 2006) will be used within Tier 2 of TREECS to compute fluxes through the vadose zone and aquifer and resulting aquifer concentrations. The scientific documentation of the MEPAS groundwater models (partially and fully saturated) is provided by Whelan et al. (1996). The following is an overview of the two models.

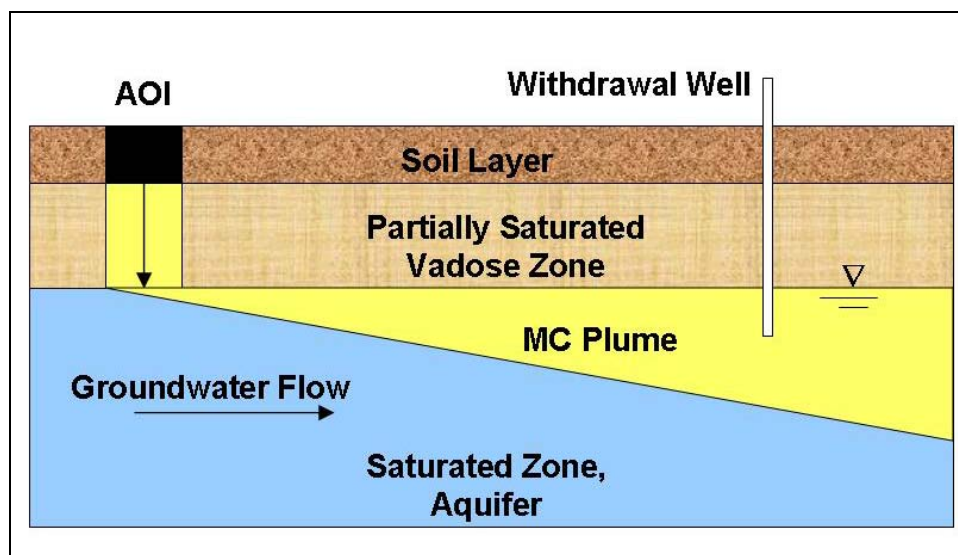


Figure 4. Site schematic of transport from soil to groundwater.

## Vadose Zone Model

The vadose model is based on the one-dimensional, advection-dispersion equation,

$$\frac{\partial C}{\partial t} + \left(\frac{w}{R_{fu}}\right)\left(\frac{\partial C}{\partial z}\right) = \left(\frac{D_z}{R_{fu}}\right)\left(\frac{\partial^2 C}{\partial z^2}\right) - \lambda C \quad (52)$$

where,

- $C$  = dissolved concentration (mg/L)
- $D_z$  = dispersion coefficient in the z direction ( $\text{cm}^2 \text{s}^{-1}$ )
- $R_{fu}$  = retardation factor for unsaturated zone (dimensionless)
- $t$  = time (sec)
- $w$  = pore water velocity in the vertical (Z) direction ( $\text{cm s}^{-1}$ )
- $z$  = distance along the vertical coordinate (cm)
- $\lambda$  = degradation or decay rate ( $\text{sec}^{-1}$ )

The retardation for the unsaturated zone is computed from

$$R_{fu} = 1 + \frac{\rho_b}{\theta_w} K_d \quad (53)$$

where,

- $\rho_b$  = bulk density ( $\text{g cm}^{-3}$ )
- $K_d$  = equilibrium partition (or distribution) coefficient ( $\text{mL g}^{-1}$ )
- $\theta_w$  = volumetric moisture content (fraction)

and

$$\theta_w = \phi \left[ \frac{K(\theta_w)}{K_s} \right]^{1/m} \quad (54)$$

where,

- $\phi$  = total porosity (fraction)
- $K_s$  = saturated hydraulic conductivity ( $\text{cm s}^{-1}$ )
- $K(\theta_w)$  = unsaturated hydraulic conductivity ( $\text{cm s}^{-1}$ )

- $m$  = coefficient dependent on soil type where  $m = 2b + 3$   
 $b$  = soil type coefficient, which is an empirical parameter relating soil matric potential and moisture content and is dependent on soil texture (Values are automatically provided from a table for soil textures within the model user interface and are viewable from the interface help file.)

If the infiltration rate is less than the saturated hydraulic conductivity,  $K(\theta_w)$  is set to the infiltration rate, and the vertical pore water flow velocity  $w$  is equal to the infiltration rate divided by  $\theta_w$ . If the infiltration rate is equal to or greater than the saturated hydraulic conductivity,  $K(\theta_w)$  is set to the saturated hydraulic conductivity  $K_s$ , and  $w$  is equal to  $K_s$  divided by  $\theta_w$ . The excess infiltration can be diverted to interflow as explained in Chapter 8. The moisture content calculated from Equation 54 is not allowed to be less than the specified soil field capacity. Thus, the moisture content varies between the field capacity and saturation, or total porosity.

The vertical dispersion is computed from

$$D_z = \alpha_z w + D_{mol} \quad (55)$$

where,

$\alpha_z$  = dispersivity in the  $z$  direction (cm)

$D_{mol}$  = molecular diffusion coefficient for solute in water ( $\text{cm}^2 \text{s}^{-1}$ )

The molecular diffusion is assumed to be negligible compared to dispersion. The dispersivity is generally proportional to the distance from the source. Thus, for computing flux through the vadose zone, this distance is the thickness of the vadose zone layer. The constant of proportionality (i.e., the factor multiplied times the vadose zone layer thickness to get  $\alpha_z$ ) is on the order of 0.01.

The vadose zone model computes the concentration entering at the top of the vadose layer to provide the boundary condition needed for the analytical solution of Equation 52. This concentration is calculated from the constituent infiltration load ( $\text{g/yr}$ ) entering the vadose zone from above divided by the percolation flow rate ( $\text{m}^3/\text{yr}$ ). The percolation flow rate is based on either the infiltration rate or  $K_s$ , whichever is smaller. The infiltration rate for the vadose zone is estimated from the infiltration flow

rate ( $\text{m}^3/\text{yr}$ ) passed to the model divided by the flow area, which is obtained from the product of the length ( $L_f$ ) and width ( $W_f$ ) of the AOI, which are passed to the model from the soil model. Thus, the percolation flow rate is either the infiltration rate or the saturated hydraulic conductivity times the flow area.

## Aquifer Model

The primary function of the aquifer model is to compute the MC concentrations within the groundwater plume. A Cartesian coordinate system is used for the plume calculation as shown in Figure 5 along with location for a withdrawal well (receptor location). The AOI source zone is also shown. The origin of the coordinate system is located at the center of the AOI vertical projection. The well is located  $x$  distance downstream from the origin or the  $Y$  axis,  $y$  distance laterally from the plume centerline ( $X$  axis), and  $z$  distance vertically from the water table surface. The model computes aquifer concentrations at the well location ( $x, y, z$ ).

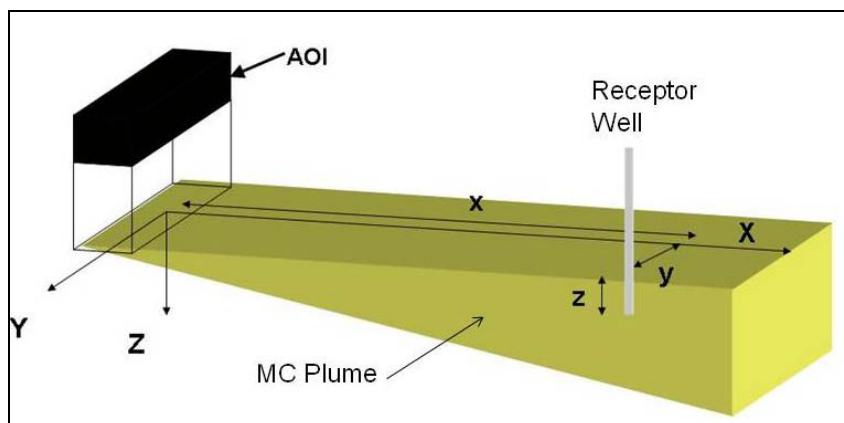


Figure 5. Plume coordinates and well location.

The MEPAS aquifer model solves the time-varying, one-dimensional advective, three-dimensional dispersive mass transport equation for solute movement through a porous medium with a unidirectional, constant or steady-state, uniform flow velocity and with first-order degradation/decay and equilibrium sorption partitioning. Other assumptions include the following:

- The groundwater environment is initially free of contamination.
- All transport media properties are homogeneous and isotropic.
- The aquifer is of finite, constant thickness and of infinite lateral extent.

- Drawdown effects of withdrawal wells and other transient stresses on the aquifer are not considered by the semi-analytical solutions.
- Flow velocities are provided by the user.
- Density differences between a contaminant plume and the natural groundwater are negligible.

The governing equation for saturated groundwater transport becomes

$$\frac{\partial C}{\partial t} + \left(\frac{u}{R_{fs}}\right)\left(\frac{\partial C}{\partial x}\right) = \left(\frac{D_x}{R_{fs}}\right)\left(\frac{\partial^2 C}{\partial x^2}\right) + \left(\frac{D_y}{R_{fs}}\right)\left(\frac{\partial^2 C}{\partial y^2}\right) + \left(\frac{D_z}{R_{fs}}\right)\left(\frac{\partial^2 C}{\partial z^2}\right) - \lambda C \quad (56)$$

where

$$R_{fs} = 1 + \frac{\rho_b}{\phi_e} K_d \quad (57)$$

and

- $u$  = pore water velocity in horizontal (X) direction (cm/sec)
- $R_{fs}$  = retardation factor in the saturated zone (dimensionless)
- $D$  = dispersion coefficients in the x-, y-, and z-directions (cm<sup>2</sup>/sec)
- $\phi_e$  = effective porosity (fraction)

All other variables have been previously defined. The pore water velocity is equal to the Darcy groundwater flow velocity divided by the effective porosity. The Darcy flow rate (m<sup>3</sup>/yr) at a specific location down-gradient is computed as the product of the Darcy velocity times the vertical and lateral extent of the plume that is continuously spreading due to lateral and vertical dispersion as it moves downstream. The Darcy flow is assumed to account for the recharge flow; hence, the recharge flow from the vadose zone is not added to the Darcy flow.

An equation analogous to Equation 55 is used to estimate  $D_x$ ,  $D_y$ , and  $D_z$ , except that  $u$  rather than  $w$  is used, and there are dispersivities for the three directions. The longitudinal dispersivity,  $\alpha_x$ , is the product of a distance and a factor. The longitudinal distance is  $x$ , the distance from the source to the well. The longitudinal dispersivity factor is on the order of 0.1. The lateral or transverse dispersivity is estimated as  $0.33\alpha_x$ . The



vertical dispersivity is estimated as  $0.0025\alpha_x$ . Effective porosity is the pore space that contributes to advective flow that is not dead-end space.

A combination of analytical and numerical methods is used to solve Equation 56 for a variety of boundary conditions, including a source influx specified over an area, such as an AOI. The solution scheme also accounts for boundary effects of aquifers of limited vertical thickness such as perched aquifers or aquifer water tables that are relatively close to bedrock.

It is noted that neither the vadose nor aquifer model allows input of initial concentrations due the legacy design of these models. This limitation is not a problem for the intended use of TREECS, which is for a source of MC contamination loading into the vadose zone from the soil.

## 6 Surface Water Models

A wide variety of surface water types may be encountered near military installations, such as streams, lakes, ponds, estuaries, and wetlands. The goal is to select a model type that can be used for any type of surface water. Two model types were considered for the Tier 1 modeling. These were the time-varying, one-dimensional, longitudinal, Contaminant Model for Streams (CMS) described by Fant and Dortch (2007), and the RECOVERY model (Ruiz and Gerald 2001), which is a time-varying contaminant model for standing or pooled surface water. The RECOVERY model was selected for Tier 1 since it provided reasonable results for both streams and lakes while restraining the complexity as desired for Tier 1. However, for Tier 2, both CMS and RECOVERY will be provided so that both flowing (streams and rivers) and standing water (ponds, lakes, wetlands, etc.) can be better represented. Each model is briefly described below.

### RECOVERY

A complete description and documentation of the RECOVERY model are presented by Ruiz and Gerald (2001). A brief description is provided here so that the differences between RECOVERY and CMS can be better contrasted. RECOVERY simulates the long-term, time-varying concentration of contaminants in surface water and bottom sediments for both dissolved and particulate contaminants. A schematic of how the water-sediment system is handled in RECOVERY is shown in Figure 6. The water column is treated as a fully mixed volume, or a continuously stirred tank reactor (CSTR). The bottom sediments are divided into two types, a surficial mixed sediment layer at the sediment-water interface, and deep sediments below the surficial mixed layer.

This treatment results in three mass balance equations with three unknowns, which apply to the water column, mixed sediment layer, and deep sediment layers. Two coupled ordinary differential equations are solved for the total (particulate and dissolved) contaminant concentration in surface water ( $C_w$ ) and in the mixed sediment layer ( $C_m$ ). A partial differential equation is solved for total concentrations over sediment depth [ $C_s(z)$ ] for the deep sediment layers. The deep sediment extends below the depth of contamination into clean sediment so that a zero concentration gradient boundary condition can be applied at the bottom of the sediment

column. Each mass balance equation accounts for mass fate processes, such as sorption, degradation, etc., which are shown in Figure 7. Equilibrium, reversible, sorption partitioning is assumed. The equations and solution schemes are documented by Ruiz and Gerald (2001).

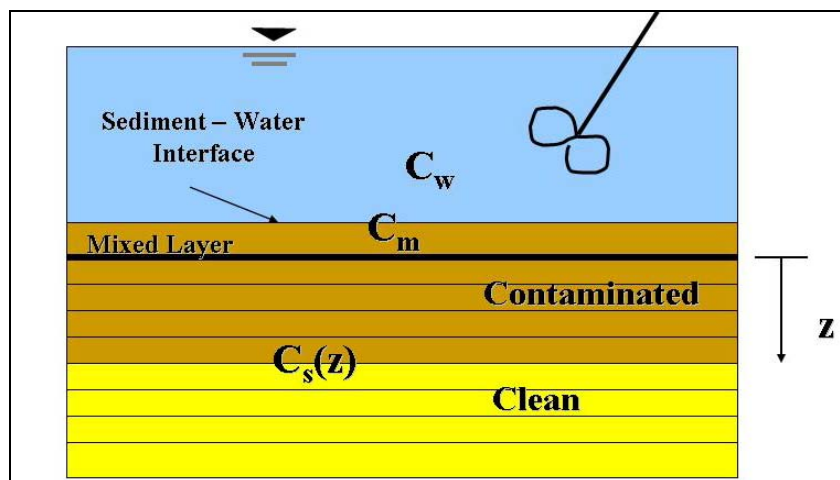


Figure 6. Schematic of the RECOVERY model.

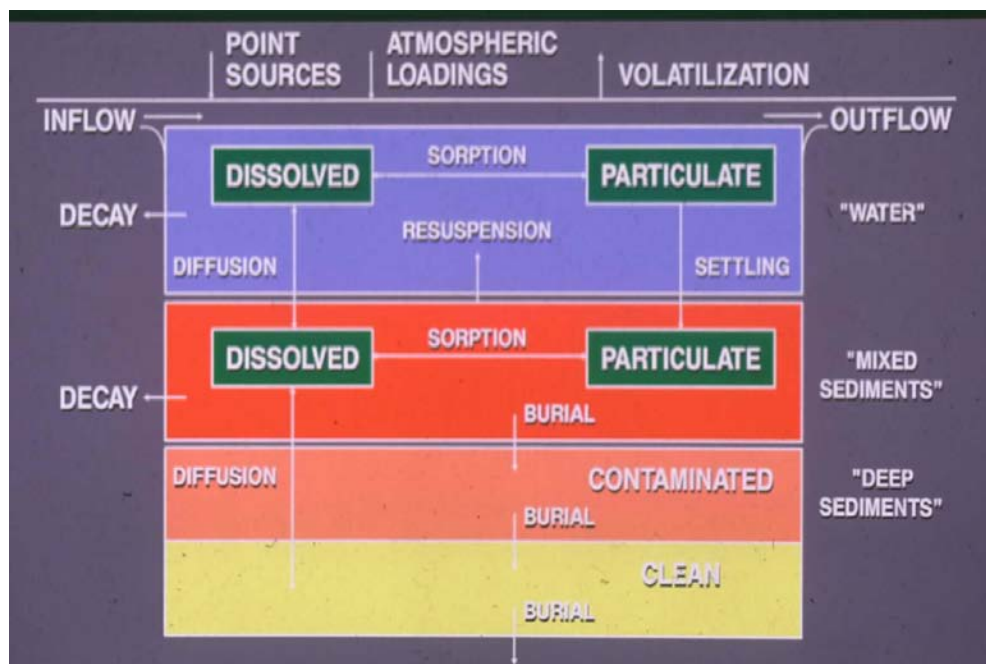


Figure 7. Fate processes within the RECOVERY model.

Loading boundary conditions include inflowing contaminant mass due to export from the soil model, which includes rainfall extraction, erosion, and interflow fluxes. There is also an option to enter a user-specified constant external loading of contaminant mass, such as those due to wastewater discharges, air deposition, or stream background loadings. Although the

model state dependent variables are total concentration, the model produces output for total and dissolved concentrations in the water column and bed via equilibrium partitioning.

## CMS

This section provides an overview of the CMS. The complete model description and documentation is provided by Fant and Dortch (2007). The CMS is a one-dimensional (1D), longitudinal, time-varying model for contaminant fate and transport in streams and rivers. The model assumes steady, uniform flow; thus, there is no hydraulic or hydrologic routing involved. Two mass balance equations-- one for the water column and one for the bed-- are solved for two unknowns, total (particulate and dissolved) contaminant concentration in the water column and in the sediment bed. Only one layer is used for the bed in this model. The model outputs total and dissolved concentrations in the water column and bed via equilibrium partitioning.

The modeled fate processes include water column advection and diffusion, partition of contaminant between sediment and water (for water column and bed), settling of particulate mass from the water column to the bed, resuspension of sediment bed mass into the water column, burial of sediment bed material, diffusion of dissolved mass across the sediment-water interface, degradation/decay, and volatilization. The model solves the one-dimensional, longitudinal advection-diffusion-reaction (mass balance) equation for the constituent concentration in the water column,

$$\begin{aligned} \frac{\partial c_w}{\partial t} + U \frac{\partial c_w}{\partial x} = D_x \frac{\partial^2 c_w}{\partial x^2} - \left( k_{dw} + \frac{k_v}{H} \right) F_{dw} c_w - k_{pw} F_{pw} c_w \\ - \frac{V_s}{H} F_{pw} c_w + \frac{V_r}{H} c_b - \frac{V_d}{H} (F_{dw} c_w - F_{db} c_b) \end{aligned} \quad (58)$$

where,

$c_b$  = concentration of the constituent in the sediment bed (M/L<sup>3</sup>),  
total mass on a total volume basis

$c_w$  = concentration of the constituent in the water column (M/L<sup>3</sup>),  
total mass on a total volume basis

$D_x$  = stream longitudinal diffusion coefficient (L<sup>2</sup>/T)

- $F_{db}$  = factor to convert to dissolved constituent concentration in the sediment bed pore water, dimensionless  
 $F_{dw}$  = fraction of the constituent dissolved in the water column, dimensionless  
 $F_{pw}$  = fraction of the constituent in particulate form in the water column, dimensionless  
 $H$  = hydraulic depth of the stream (L)  
 $k_{dw}$  = decay rate of dissolved constituent in the water column (T<sup>-1</sup>)  
 $k_{pw}$  = decay rate of particulate constituent in the water column (T<sup>-1</sup>)  
 $k_v$  = stream volatilization rate of the constituent (L/T)  
 $t$  = time (T)  
 $U$  = stream mean velocity (L/T)  
 $V_d$  = mass transfer rate across the sediment-water interface resulting from diffusion of the dissolved constituent (L/T)  
 $V_r$  = sediment resuspension rate (L/T)  
 $V_s$  = suspended solids settling rate (L/T)  
 $x$  = downstream distance along stream (L)

The stream reach is sub-divided into computation nodes spaced equal distance apart along the stream longitudinal axis,  $x$ . Equation 58 is solved for each computation node. The sediment bed is represented as a single homogeneous active layer (i.e., a CSTR) underneath each water column node. The mass balance equation for each nodal bed layer is

$$\begin{aligned} \frac{dc_b}{dt} = & -(k_{db}F_{db} + k_{pb}F_{pb})c_b + \frac{V_d}{h}(F_{dw}c_w - F_{db}c_b) \\ & - \frac{V_r}{h}c_b + \frac{V_s}{h}F_{pw}c_w - \frac{V_b}{h}c_b \end{aligned} \quad (59)$$

where,

- $F_{pb}$  = fraction of constituent in particulate form in the bed  
 $h$  = active sediment layer thickness (L)  
 $k_{db}$  = decay rate of dissolved constituent in bed pore water (T<sup>-1</sup>)  
 $k_{pb}$  = decay rate of particulate constituent in the bed (T<sup>-1</sup>)  
 $V_b$  = active sediment layer burial rate (L/T)

All other variables have been defined. Longitudinal exchange between adjacent bed segments, such as pore water flow or diffusion along the stream flow axis within the bed, is assumed to be negligible.

The factor and fractions in Equations 58 and 59 are defined as follows,

$$F_{dw} = \frac{1}{1 + K_{dw}S} \quad (60)$$

$$F_{pw} = \frac{K_{dw}S}{1 + K_{dw}S} \quad (61)$$

$$F_{db} = \frac{1}{\phi + K_{ds}(1 - \phi)\rho_s} \quad (62)$$

$$F_{pb} = \frac{K_{ds}(1 - \phi)_s}{\phi + K_{ds}(1 - \phi)_s} \quad (63)$$

where,

$K_{dw}$  = sediment-water partitioning coefficient for the constituent in the water column ( $L^3/M$ )

$K_{ds}$  = sediment-water partitioning coefficient for the constituent in the sediment bed ( $L^3/M$ )

$S$  = TSS concentration ( $M/L^3$ )

$\phi$  = porosity of the sediment bed, fraction

$\rho_s$  = dry sediment particle density ( $M/L^3$ )

Constituent partitioning between sediment and water is assumed to be in equilibrium, linear, and reversible. The model can only be applied to a single reach where hydraulic properties ( $U$ ,  $D_x$ , and  $H$ ) are assumed to be constant and uniform.

The model allows either direct input of the volatilization rate or calculation of it based upon Henry's Law and Whitman's two-film theory (Chapra 1997) as modified for the influence of water flow and wind as described by Fant and Dortch (2007). Mass transfer rate of dissolved constituents across the sediment-water interface is calculated based upon flow conditions, molecular diffusivity and other factors as described by Fant and Dortch (2007).

A single active sediment layer is modeled. The active bed layer is assumed to have constant properties, thus, the thickness, volume, porosity, bulk density, and solids mass are constant over time (i.e., steady-state) and assumed to be uniform over the stream reach. Solids and contaminant mass that are buried to deep sediments are assumed to be lost. Performing a steady-state solids balance for the bed layer results in the following relationship,

$$V_b = \frac{V_s S}{\rho_b} - V_r \quad (64)$$

where all variables have been previously defined. The dry bulk density of the bed  $\rho_b$  can be computed from  $(1 - \phi) \rho_s$ . By specifying any two of the sedimentation rate terms in Equation 64 along with the bulk density and TSS (S), the remaining rate term can be solved. The three sedimentation process rates of Equation 64 are applied throughout the modeled stream reach along with a constant and uniform value of S.

An implicit, finite difference, numerical solution scheme, based on a variation of the Crank-Nicolson (CR) method (Chapra 1997), is used to solve the partial differential equation for surface water contaminant concentration (Equation 59). The CR scheme is unconditionally stable even for large time steps and reduces numerical dissipation. A choice between two numerical integration schemes, Euler and fourth order Runge-Kutta, is provided to solve the ordinary differential equation for sediment bed contaminant concentration (Equation 59). An adaptive time-stepping solution option has been implemented for solving the ordinary differential equation for the bed to ensure stable results.

The CMS has been verified against known analytical solutions (Fant and Dortch 2006) and the RECOVERY model (Fant and Dortch 2007). The main reason for using CMS is for cases where there may be sediment and water contaminant concentrations that vary along the stream reach and over time. Although the CMS was developed for long-term fate of contaminants in sediment and water, it can also be used to assess short-term spill events or transient, storm-water transport. The CMS is also better suited than the RECOVERY model for streams that are tidally influenced since it is 1D and includes diffusion/dispersion, which can be used to represent tidal mixing in 1D models through tidal dispersion (Thomann 1972, Fischer et al. 1979).

## 7 Model Implementations

The Tier 2 soil model will generate outputs (export mass fluxes) that are used by the vadose zone model and the surface water model (RECOVERY or CMS). The vadose zone model will generate output that is used by the aquifer model. If groundwater discharge is included, then the aquifer model will generate output that is used by the surface water model.

This chapter discusses the input requirements for each model and how those are addressed for Tier 2 analyses. Model outputs are also discussed. No additional assumptions or simplifications are made for the receiving water models (vadose, aquifer, and surface water) in Tier 2. Thus, the user will have full control to use the entire capabilities of each receiving water model.

### Soil Model

The soil model described in Chapter 4 has the input requirements listed in Table 1. A user interface will be developed for the Tier 2 soil model for setting up, reviewing, and editing model inputs.

There will also be several options in the soil model user interface that the user will be able to choose when applying the soil model. One option will be to include or not include solid phase particle erosion (i.e., Equation A7 for the flux term in Equation 2). Within the user interface, the user can use solubility values that are passed from the constituent database or input user specified values. For RDX and TNT solubility, there will also be the option of computing it from Equations 44 and 45. The user will have the option to calculate or input a user-specified volatilization rate  $K_v$  within the user interface. If the calculate option is chosen, then the user will also have the option of changing the default value for  $d_v$  (used in calculating the volatilization rate) and using the estimated diffusion rate in air, a database value, or a specified a value.

The variables listed in Table 1 are discussed in Chapter 4. These variables fall into five categories including: site characteristics, soil properties, hydrology, fate/transport parameters, and chemical-specific properties. The sources of data and methods for estimating these inputs are discussed below.



Table 1. Tier 2 soil model inputs.

Parameter	Units	Description
Site Characteristics		
$L_f$	m	AOI dimension that is parallel to the groundwater flow (This variable is not actually used by the soil model, but it will be read by the soil model user interface since it is required by and will be passed to the vadose and aquifer models.)
$W_f$	m	AOI dimension that is perpendicular to the groundwater flow (This variable is not actually used by the soil model, but it will be read by the soil model user interface since it is required by and will be passed to the vadose and aquifer models.)
A	m <sup>2</sup>	AOI surface area
$Z_b$	m	Active soil layer thickness
$T_{\text{soil}}$	°C	Average annual temperature of the soil-water matrix, which is used for all temperature dependent calculations
L	g/yr	MC mass residue loading versus time
$C_s(0)$	mg/kg	Initial solid phase MC concentration in soil on a soil mass basis at time 0, which must be input for each MC that is modeled (This variable will be converted by the soil model user interface to solid phase MC mass, g, in soil for use in the soil model.)
$C_{ns}(0)$	mg/kg	Initial total non-solid phase MC concentration in soil on a soil mass basis at time 0, which must be input for each MC that is modeled (This variable will be converted by the soil model user interface to non-solid phase MC concentration in soil on a total volume basis, g/m <sup>3</sup> , for use in the soil model.)
Soil Properties		
$\theta_w$	fraction	Volumetric soil moisture content
$\rho_b$	g/cm <sup>3</sup>	Soil dry bulk density
$\phi$	fraction	Soil porosity
Hydrology		
P	m/yr	Average annual precipitation
$P_r$	m/yr	Average annual rainfall
E	m/yr	Average annual soil erosion rate
$q_w$	m/yr	Average annual water infiltration rate through soil compartment; rate of vertical water movement through soil after ET and runoff losses (equal to groundwater recharge for no interflow)
$q_r$	m/yr	Average annual surface water runoff rate
$F_{if}$	fraction	Fraction of annual water infiltration flow rate and mass flux that goes to soil interflow
N	yr <sup>-1</sup>	Average number of rainfall events per year

Parameter	Units	Description
Fate/Transport Parameters		
$K_d$	L/kg	Soil-water constituent partition coefficient, which must be input for each MC that is modeled (Options for estimating this parameter will be provided in the user interface.)
$d_e$	m	Soil exchange layer thickness for rainfall ejection of pore water
$a$	Kg/L	Soil detachability for rainfall ejection of pore water
$\lambda_l$	yr <sup>-1</sup>	Decay/degradation rate of liquid (water) phase constituent, which must be input for each MC that is modeled
$\lambda_a$	yr <sup>-1</sup>	Decay/degradation rate of adsorbed (particulate) phase constituent, which must be input for each MC that is modeled
$d_i$	μm	Initial mean diameter of solid phase constituent residue particles, which must be input for each MC that is modeled
$K_v$	m/yr	Volatilization rate, which must be input for each MC that is modeled (The soil model user interface will have the option to compute or specify this parameter, and the value will be passed to the soil model. If this parameter is computed, then the diffusion layer thickness $d_v$ (m) will also be required as input in the user interface.)
$d_v$	m	Diffusion layer thickness in the upper soil horizon, which is required for computing volatilization rate in the soil model user interface (The default value is 0.4 m).
$x$	dimensionless	Particle shape index, which is used to specify for the soil model whether cylindrical (index = 1) or spherical (index = 2) solid phase particles are being considered for each modeled MC (A value must be input for each MC that is modeled.)
Chemical-specific Properties		
$C_s$	mg/L	Aqueous solubility limit, which must be input for each MC that is modeled
$H_e$	atm•m <sup>3</sup> /g•mol	Henry's law constant, which must be input for each MC that is modeled (This property will be converted by the user interface to dimensionless units for use by the soil model.)
MW	g/mol	Molecular weight (molar mass or average molecular mass), which must be input for each MC that is modeled (This variable is not required by the soil model, but it will be required by the soil model user interface for computing volatilization rate, which is required by the model.)
$\rho_{sm}$	g/cm <sup>3</sup>	Solid phase constituent mass density, which must be input for each MC that is modeled

### Site Characteristics

The AOI dimensions and surface area can be decided within the GIS module of TREECS or other similar external means. The area of the AOI ( $A$ ) used in the soil model is not necessarily equal to the product of the length ( $L_f$ ) and width ( $W_f$ ) of the AOI. Figure 8 shows a hypothetical AOI with site dimensions. Both length dimensions are required for the vadose and aquifer models and are passed to them. The AOI width should be perpendicular to the groundwater flow direction and should extend across the full AOI area. It can generally be assumed that groundwater flow and runoff flow are in roughly the same direction. The AOI length is perpendicular to the width. The AOI area  $A$  is used by the soil model and must be computed using GIS or other methods if the AOI is an irregularly shaped polygon.

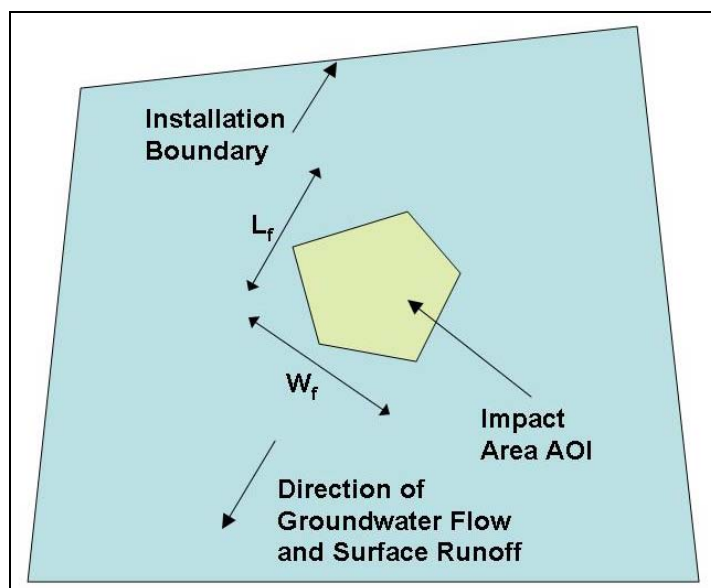


Figure 8. AOI dimensions.

The active soil layer thickness  $Z_b$  is the upper soil horizon where most of the MC mass residue is believed to reside. In general, this thickness can be on the order of a meter or less. A default value for  $Z_b$  of 0.4 m is suggested, since this is the recommended soil diffusion layer thickness for computing volatilization rates (See Chapter 4).

The average or mean annual temperature of the soil-water matrix of the active soil layer is required to compute the dimensionless Henry's constant for ambient conditions and solubility when a function relating solubility and temperature is available, such as for TNT and RDX. Mean annual soil and soil-water temperature are assumed to be the same and can be

estimated by adding 1 °C to the mean annual air temperature, which can be computed from daily average air temperatures within the HGCT.

MC mass residue loadings are required and are passed from the MC residue loading model discussed in Chapter 3. Additionally, the user must input the initial soil concentrations for both solid (pure product) and non-solid phase (weathered) MC. These concentrations should be on a soil mass basis (mg/kg), which is usually how soil concentrations are reported. The solid phase mass balance equation requires mass rather than concentration. Therefore, the soil model user interface must convert the solid phase (pure product) mass concentration into mass (g) units by multiplying the input initial pure product concentration by the soil dry bulk density, soil layer thickness, and AOI surface area. The non-solid phase (weathered) mass balance equation requires concentration on a soil volume basis (g/m<sup>3</sup>); thus, the soil model user interface must multiply the input initial weathered concentration by the soil dry bulk density. In many cases, the user will input zero for both initial concentrations. When there is reason to input non-zero values, such as when the initial MC total (pure product plus weathered phase) concentration in soil has been measured, then the user must decide how to split the concentration between pure product and weathered phases. Since soil and pure product MC particles usually have different particle densities, a gravimetric separation technique may be required to measure the pure product and weathered MC concentrations. In the absence of special analyzing techniques, the split between the two types of MC may have to be based on a guess or best estimate.

### Soil Properties

Site-specific soil properties,  $\theta_w$ ,  $\rho_b$ , and  $\phi$ , can be estimated based upon soil texture, such as silty loam, sandy clay loam, etc. (see Dortch et al. 2009). Bulk density is related to dry soil particle specific weight or density  $\rho_s$  and soil porosity according to the relationship  $\rho_b = (1 - \phi)\rho_s$ . The value of  $\rho_s$  is typically about 2.65 g/cm<sup>3</sup>. Soil texture tables include field capacity rather than moisture content, but field capacity can be used as an estimate for  $\theta_w$  in partially saturated surface soils since the water content tends to fluctuate above and below the field capacity over the period of a year. The mean particle diameter of the soil can also be estimated from soil texture if needed later. The Hydro-Geo-Characteristics toolkit (HGCT) within TREECS includes tools for estimating soil properties.

## Hydrology

The methods being built into the HGCT for estimating the average annual hydrologic variables ( $P$ ,  $P_r$ ,  $E$ ,  $q_w$ ,  $q_r$ , and  $N$ ) are presented by Dortch et al. (2009 and 2010). The average annual infiltration ( $q_w$ ) and runoff ( $q_r$ ) rates are multiplied by the AOI area in the soil model interface to obtain flow rates needed by the downstream models. It is noted that the runoff is not actually used in the soil model computations, but the runoff flow rate ( $\text{m}^3/\text{yr}$ ) is calculated and written to the WFF surface water output file as this information can be consumed by downstream surface water models, such as CMS. Infiltration rate ( $\text{m}/\text{yr}$ ) is needed by the soil model and infiltration flow rate ( $\text{m}^3/\text{yr}$ ) is required by the vadose zone model; therefore, the infiltration flow rate is written to the WFF vadose output file.

Rainfall is precipitation that occurs above 0 °C. The hydrologic methods in the HGCT require a long-term (20 years or more), historical record of daily precipitation and monthly average air temperatures. Monthly average air temperatures can be developed from daily average values.

The fraction of infiltration flow and mass flux that goes into soil interflow, which is diverted to surface water, can be specified by the user based upon their best judgment, or it can be computed by the soil model user interface if a value for the saturated hydraulic conductivity for the vadose zone below the soil layer is provided. The method for computing the interflow fraction is explained in Chapter 8. Interflow water flow rate is added to the runoff flow rate and subtracted from infiltration flow rate for output. Likewise, the interflow mass flux is subtracted from the leaching flux and added to the pore water extraction/runoff flux.

## Fate/Transport Parameters

There will be several options for selecting  $K_d$ . An estimator will be built into the Tier 1 and 2 soil models' user interfaces for estimating  $K_d$  for organic constituents. The estimator (Streile et al. 1996) is based on soil texture (percentages of sand, silt, and clay) along with percent organic matter and the organic carbon to water partitioning coefficient ( $K_{oc}$ ), which can be estimated from the octonol-water partitioning coefficient ( $K_{ow}$ ) if not available. The estimator is stated as,

$$K_d = 0.0001 K_{oc} (57.735 OM + 2.0 clay + 0.4 silt + .005 sand) \quad (65)$$

where OM is the percent by weight of organic matter in the soil. If  $K_{oc}$  is not known but  $K_{ow}$  is known,  $K_{oc}$  can be estimated with  $K_{oc} = 0.617 f_{oc}$ , where  $f_{oc}$  is the fraction by weight of organic carbon in the soil. Soil organic carbon is about 58 percent of soil organic matter; thus,  $f_{oc} = 0.0058 OM$ .

There also will be a look up table capability for a limited number of inorganic constituents that provides  $K_d$  as related to soil pH, percent clay, percent OM, and percent iron and aluminum oxyhydroxides (Streng et al. 1989). If there are soil  $K_d$  values in the constituent database, those can be selected as well. User-specified values for  $K_d$  can also be input.

Default values will be provided for four of the other fate/transport parameters with the option for the user to change each. The default values will be 0.005 m, 0.4 kg/L, 0.0 yr<sup>-1</sup>, and 0.0 yr<sup>-1</sup> for  $d_e$ ,  $a$ ,  $\delta_i$ , and  $\delta_a$ , respectively. The values for  $d_e$  and  $a$  are in the range of values reported by Gao et al. (2004). Zero degradation rates are for conservative conditions of no degradation. Help files will be available for estimating degradation rates in soil if non-zero values are used. These help files will be based on information from various reports (Jenkins et al. 2003, Miyares and Jenkins 2000, Mulherin et al. 2005, Gerald et al. 2007, and Dortch et al. 2005). Additionally, the constituent databases, especially the Army Range Constituent Database (ARCDB), may have degradation half-lives for MC in soil. If there is a soil half-life, the soil model user interface will pull that value into the application, but the user can change the value if he or she desires. The soil model uses degradation rates (yr<sup>-1</sup>), but the soil model interface takes the input as degradation half-life (yr) and converts to a rate using  $\lambda = \frac{0.693}{t_{1/2}}$ , where  $t_{1/2}$  is half-life (see Equation 66). It should be

recognized that much of the information on degradation rates is based on laboratory studies. Some sites can experience lower degradation rates than reported from laboratory studies (Dortch et al. 2007).

Solid phase particle sizes can vary widely for various types of munitions and for a particular MC. Help files will be provided regarding solid phase MC particle sizes for setting  $d_i$ . These help files will be based on information from various reports (Larson et al. 2005, Pennington et al. 2005, and Taylor et al. 2004).

There will be a feature within the soil model user interface allowing the user to either specify a value or estimate a value for the volatilization rate

for each MC using Equations 46 and 48. Of course the volatilization rate for inorganic MC should be set to zero. There won't be any gas phase existing in the soil for inorganic MC since Henry's constant is zero; thus, there should not be any volatilization even if the rate is not set to zero. If the volatilization rate is computed, then the MC diffusivity in air must be specified. If a value of the MC diffusivity in air exists in the constituent database, that value will be provided; and if not, a value will be provided using Equation 47. In either case, the user can over-ride the provided value and enter his or her value. Additionally, the user will be able to either specify the soil diffusion layer thickness for the volatilization rate calculation or use the default value of 0.4 m.

The particle shape index is used to specify for the soil model whether cylindrical (index = 1) or spherical (index = 2) solid phase particles are being considered for each modeled MC. For cylindrical and spherical particles, Equations 41 and 42, respectively, are used by the soil model to compute particle average specific surface area. The value of  $x$  in the exponent of Equation 43 is 2 for cylindrical and 3 for spherical particles. In most cases, spherical particles should be used. The primary reason for providing cylindrical particles is for investigating the effect of particle shape on computed results. However, cylindrical particles may be better suited for modeling metal projectiles on SAFRs.

### **Chemical-Specific Properties**

Constituent chemical-specific properties will be provided for the most part by databases that will be available within TREECS. There will be four options for selection of a chemical database for use in an application. One option is to use the Army range constituent database (Zakikhani et al. 2002 and Dortch et al. 2005). The Army range constituent database (ARCDB) can include multiple values for chemical-specific properties, so a viewer/editor is required and will be provided in TREECS to show the user each value and will require selection of a value to use for each property and for each MC. The older version of the ARCDB has been recently updated during the TREECS project to fit the new specifications and schema outlined by Dortch et al. (2005). Additionally, a search for additional property values is being conducted for priority MC to help ensure that values will be available.

The Framework for Risk Analysis in Multimedia Environmental Systems (FRAMES) (Whelan et al. 1997) database (<http://mepas.pnl.gov/FRAMESV1/mmede.stm>) and the Risk Assessment Information System (RAIS) constituent database

(<http://rais.ornl.gov/index.shtml>) will also be available in TREECS for specifying constituent chemical-specific properties. The fourth option will be to use a user-defined database. User-defined constituent databases are based on the FRAMES constituent database format. A constituent database editor will be provided within TREECS tools for developing and editing user-defined constituent databases.

Database values for solubility of organic MC are fairly reliable. Solubility of metals is highly dependent on the site soil geochemistry. The equilibrium chemistry model Visual Minteq is being applied for estimating metal solubility given soil-water ion (such as carbonate, sulfate, chloride, calcium, magnesium, and potassium) concentrations and other soil chemistry information. The results of the investigation of using Visual Minteq will be presented in another follow-on report to this report.

## Output

Output of the Tier 2 soil model will consist of time series of each of the following computed variables for each MC:

- Solid phase MC mass (g) in AOI soil,  $M_s$
- Non-solid phase mass (g) in AOI soil,  $M_{ns}$
- Non-solid phase MC total (dissolved, adsorbed, and vapor) concentration in AOI soil on a total soil volume basis ( $\text{g}/\text{m}^3$ ),  $C_{tt}$
- Non-solid phase MC dissolved concentration in AOI soil on a water volume basis ( $\text{g}/\text{m}^3$ ),  $C_l$
- Total MC concentration (solid and non-solid phases) in AOI soil on a soil mass basis ( $\text{mg}/\text{kg}$ ),  $C_{Ts}$ . These concentrations should be provided via a Soil Concentration File (SCF) according to the FRAMES specifications. Additionally, the concentrations  $C_l$  should be provided via a SCF according to the FRAMES specifications. FRAMES is used as the underlying modeling framework that provides the mechanisms for interfacing disparate models. The user needs to understand nothing more than this about FRAMES.
- Mass fluxes ( $\text{g}/\text{yr}$ ) including:
  - Dissolution,  $F_{dis}$
  - Solid phase erosion,  $F_{es}$
  - Non-solid phase erosion,  $F_e$
  - Leaching,  $F_l$
  - Rainfall induced pore water ejection and runoff,  $F_r$
  - Degradation,  $F_{decay}$



- Volatilization,  $F_{vol}$
- Vadose WFF MC mass flux, g/yr, according to the FRAMES specifications. The flux to vadose will consist of  $F_l$  less the portion lost to interflow flux.
- Surface water WFF MC mass flux (g/yr) as adsorbed (particulate) and dissolved according to the FRAMES specifications. Particulate flux will consist of a combination of  $F_{es}$  plus a portion of  $F_e$ , and dissolved flux will consist of  $F_r$  plus a portion of  $F_e$  plus the interflow portion of  $F_l$ .

Additionally, the soil model output will include:

- Vadose WFF water flux (percolation flow),  $m^3/yr$ , according to the FRAMES specifications. Percolation flow rate (water flux) is computed from  $q_w(1 - F_{if})A$ .
- Surface water WFF water flux (runoff and interflow),  $m^3/yr$ , according to the FRAMES specifications. Surface water flow rate (water flux) is the sum of the runoff flow rate and interflow flow rate. The runoff flow rate is the product of the average annual runoff depth and the AOI area  $A$ . The interflow flow rate is the product of the average annual infiltration rate, the fraction diverted to interflow, and the AOI area, or  $q_w F_{if} A$ .

## Vadose Zone Model

The input parameters of the MEPAS vadose zone model are listed in Table 2. The inputs are divided into categories according to the input screens of the user interface as shown in Figure 9. The parameter names as identified within the model are shown in parenthesis in the table. The units shown in the table are the standard units for model input. However, the MEPAS models allow multiple input units, and the units that are input are automatically converted to standard units required for the model.

The AOI length dimensions have been discussed previously for the soil model. These soil model inputs are passed to the vadose zone model. The groundwater recharge flow rate  $Q_w$  is simply the net infiltration rate, or percolation rate, which is  $q_w(1 - F_{if})$ , times the AOI surface area, all of which were input to the soil model. The variable  $F_{if}$  is the fraction of

Table 2. MEPAS vadose zone model input parameters.

Parameter	Units	Description
Inputs passed from soil model		
$L_f$	m	AOI dimension that is parallel to the groundwater flow
$W_f$	m	AOI dimension that is perpendicular to the groundwater flow
WFF aquifer water flux, $Q_w$	$m^3/yr$	Water flow rate due to net infiltration, or percolation, from soil (groundwater recharge into vadose zone)
WFF aquifer mass flux, $(1 - F_{if})F_i$	$g/yr$	MC mass flux versus time due to leaching from soil to vadose zone, which is the total leaching flux $F_i$ times $(1 - F_{if})$ , where $F_{if}$ is the fraction of infiltration flow that goes to interflow
Soil Composition		
WP-SAND	Percent	Percentage of sand
WP-SILT	Percent	Percentage of silt
WP-CLAY	Percent	Percentage of clay
WP-OMC	Percent	Percentage of organic matter
WP-IRON	Percent	Percentage of iron and aluminum
Characteristics		
pH (WP-PH)	pH units	pH of pore water
$\phi$ (WP-TOTPOR)	fraction	Total porosity
$\theta_f$ (WP-FIELDCL)	Percent	Field Capacity
$K_s$ (WP-CONDUCT)	cm/day	Saturated hydraulic conductivity
$Z_v$ (WP-THICK)	cm	Thickness of the vadose zone layer
$\alpha_z$ (WP-LDISP)	cm	Longitudinal (vertical direction) dispersivity
$\rho_b$	$g/cm^3$	Soil dry bulk density
Constituent Properties		
$K_d$ (WA-SUBKD)	ml/g	Adsorption (partition) coefficient
$C_s$ (WP-(R)SOL)	mg/L	Water solubility of constituent
$T_{1/2}$ (WP-GHALF)	days	Half-life of constituent in vadose zone

Soil class - WP-CLASS		
Percentage of sand - WP-SAND *	81 %	Ref: 0
Percentage of silt - WP-SILT *	11 %	Ref: 0
Percentage of clay - WP-CLAY *	6 %	Ref: 0
Percentage of organic matter - WP-OMC *	2 %	Ref: 0
Percentage of iron and aluminum - WP-IRON *	0 %	Ref: 0
Soil type coefficient - WP-SOILCOEF	4.38	Ref: 0

\* The percent of sand, silt, clay, organic matter, and iron must add up to 100%

Figure 9. MEPAS vadose model user interface.

infiltration flow that goes to interflow. The MC mass flux due to leaching from soil that enters the vadose zone is  $F_l (1 - F_{if})$ , where  $F_l$  is the total soil leaching flux. The soil model wrapper will compute the water and mass fluxes entering the vadose zone and pass them the vadose zone model in the form of an vadose water flux file (WFF).

## Inputs Passed from Soil Model

### Soil Composition

Soil composition includes soil texture (percentage of sand, silt, and clay), percentage of organic matter (OM), and combined percentage of iron and aluminum. The five percentages must total 100 percent. The MEPAS models include a utility called Soil Class for selecting the soil texture. The user interface for this utility is shown in Figure 10. Given the selection of a texture, the percentages of sand, silt, and clay are automatically filled into the data boxes in the user interface screen. The soil texture is used to automatically set most of the parameters on the Characteristics screen.

Percent of soil organic matter can be estimated as  $OM = 1.72 OC$ , where OC is the percent of soil organic carbon by weight (g organic carbon/g soil x 100). Thus, OM can also be estimated from  $OM = 172 f_{oc}$ , where  $f_{oc}$  is the fraction by weight of organic carbon in the soil. Organic matter is used for

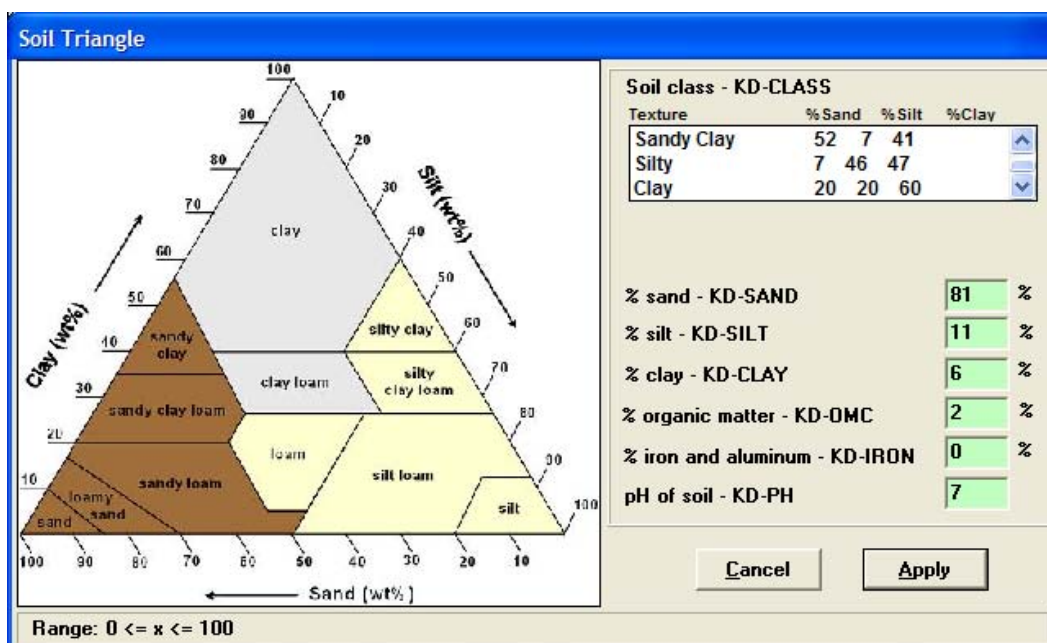


Figure 10. MEPAS model utility for selecting soil texture.

estimating  $K_d$ . Iron and aluminum content refers to oxyhydroxides, which are important relative to sorption partitioning for some inorganic constituents. There is a data table with lookup feature in TREECS that relates  $K_d$  (for a select list of inorganic constituents) to soil pH and the summed percentage by weight of clay, organic matter, and iron + aluminum content in the soil. This feature was briefly described for the soil model inputs. If only organic MC are of interest, the percent of iron + aluminum can be set to zero.

The soil type coefficient is also shown on the composition input screen, but this value is automatically filled in when the soil texture is completed, although the user can change it. The user must also input the pH of the soil pore water for use in computing  $K_d$  for inorganic constituents that are in the inorganic database as explained above. Thus, the value of pH is only used for estimating  $K_d$  of inorganic MC that are in the lookup table described above.

### Characteristics

Once the soil composition screen is complete through the use of the soil class input screen, all but two of the parameters on the characteristics screen are automatically filled in based upon tables that relate soil properties to soil texture (Dortch et al. 2009). The user can change any of the soil properties on the characteristics screen.

The thickness of the vadose zone layer must be input by the user. This thickness should be the depth from the top of the vadose zone to groundwater, since TREECS Tier 2 limits the vadose zone to a single layer. It should be noted that the user can select the units of input, which is true of most all of the MEPAS model inputs.

The user must also input the longitudinal dispersivity, which is actually in the vertical direction for the vadose zone model. This dispersivity should be approximately 0.01 times the vadose zone layer thickness. The MEPAS models, as well as the other models within TREECS, have help files accessible from the user interface to help in providing inputs.

### **Constituent Properties**

Like the soil model, there are several options for entering the soil partitioning coefficient  $K_d$ . One option is to simply enter a user-specified value. Another option is to use the value in the constituent database if a value is present in the database. Another option is to estimate  $K_d$  based upon soil composition. This option uses Equation 65 for organic constituents or the look up table for inorganic constituents as explained above and as used by the soil model.

Water solubility will be passed to the model interface from the constituent database that is used within TREECS if a value is available in the database. If not, the user must enter the solubility.

The user must enter the half-life in vadose zone. Any values of half-life in soil may be appropriate for the vadose zone as well. Half-life is related to decay rate  $\lambda$  (time<sup>-1</sup>) according to the formulation

$$T_{1/2} = \frac{0.693}{\lambda} \quad (66)$$

where the time units (e.g., days, years, etc.) can be selected by the user. For conservative forecasts, the half-life in the vadose zone could be set at a large number, such as 1.0E20 years, which would essentially be no degradation.

## **Output**

The output for the MEPAS vadose zone model include time series of Aquifer WFF water flux ( $\text{m}^3/\text{yr}$ ) due to groundwater recharge and Aquifer WFF MC mass flux out ( $\text{g}/\text{yr}$ ) associated with percolation. This mass flux is output for each MC. These files are viewable via a suite of viewers developed for FRAMES.

## **Aquifer Model**

The input parameters of the MEPAS vadose zone model are listed in Table 3. The inputs are divided into categories according to the input screens of the user interface as shown in Figure 11. The parameter names as identified within the model are shown in parenthesis in the table. The units shown in the table are the standard units for model input. However, the MEPAS models allow multiple input units, and the units that are input are automatically converted to standard units required for the model.

### **Inputs Passed from the Vadose Zone Model**

The variables passed from the vadose model are the same as those passed from the soil model to the vadose zone model, except that the mass fluxes have been modified by fate/transport through the vadose zone. Retardation and degradation can greatly alter and attenuate the time series of mass flux from soil as it is passed through the vadose zone.

### **Composition**

Soil composition is input in the same manner as for the vadose zone model where the utility is available in the user interface for selecting soil texture. The groundwater soil composition can be set differently from the surface soil and vadose zone.

### **Characteristics**

The percent of constituent flux entering the aquifer is usually set to 100 percent for conservatism in predictions. Values less than 100 percent are intended to represent interflow that goes to surface water rather than groundwater. However, recall that interflow will be handled by the soil model in TREECS before infiltration flux enters the vadose zone. Thus, interflow will have already been taken into account, and the percentage entering the aquifer from the vadose zone should be set to 100.

Table 3. MEPAS aquifer model input parameters.

Parameter Name	Units	Description
Inputs passed from vadose zone model		
$L_f$	m	AOI dimension that is parallel to the groundwater flow
$W_f$	m	AOI dimension that is perpendicular to the groundwater flow
WFF aquifer water flux	m <sup>3</sup> /yr	Water flow rate due to percolation through the vadose zone; i.e., groundwater recharge
WFF aquifer mass flux	g/yr	MC mass flux versus time due to percolation from the vadose zone to the aquifer
Composition		
WZ-SAND	Percent	Percentage of sand
WZ-SILT	Percent	Percentage of silt
WZ-CLAY	Percent	Percentage of clay
WZ-OMC	Percent	Percentage of organic matter
WZ-IRON	Percent	Percentage of iron and aluminum
Characteristics		
WZ-FRAC	Percent	Percentage of constituent flux entering the aquifer
WZ-PH	Dimensionless	pH of the pore water
$\phi$ , WZ-TOTPOR	Percent	Total porosity
$\phi_e$ , WZ-EFFPOR	Percent	Effective porosity
$V_d$ , WZ-PVELOC	cm/day	Darcy velocity
$Z_A$ , WZ-THICK	cm	Thickness of aquifer
$\rho_b$ , WZ-BULKD	g/cm <sup>3</sup>	Soil dry bulk density
Concentration Locations		
$x$ , WZ-DIST	cm	Longitudinal distance to well
$y$ , WZ-YDIST	cm	Perpendicular distance from plume center-line to well
$z$ , WZ-AQDEPTH	cm	Vertical distance below water table to well intake
$\alpha_x$ , WZ-LDISP	cm	Longitudinal dispersivity
$\alpha_y$ , WZ-TDISP	cm	Transverse dispersivity
$\alpha_z$ , WZ-VDISP	cm	Vertical dispersivity
Flux Locations		
$x$ , WZ-DIST	cm	Longitudinal distance to flux location
$\alpha_x$ , WZ-LDISP	cm	Longitudinal dispersivity
$\alpha_y$ , WZ-TDISP	cm	Transverse dispersivity
$\alpha_z$ , WZ-VDISP	cm	Vertical dispersivity
Constituent Properties		
$K_d$ , WA-SUBKD	ml/g	Sorption partitioning coefficient
$C_s$ , WZ-RSOL	mg/L	Water solubility
$T_{1/2}$ , WZ-GHALF	days	Half-life of constituent in groundwater

MEPAS Aquifer Module - aqu19

File Reference Options Help

Composition | Characteristics | Concentration Locations | Flux Locations | Constituent Properties

Usage location: well 1 (exp20)

Longitudinal distance to well - WZ-DIST: 2 km Ref: 0

Perpendicular distance from plume center line to well - WZ-YDIST: 0 cm Ref: 0

Vertical distance below water table to well intake - WZ-AQDEPTH: 100 cm Ref: 0

Longitudinal dispersivity - WZ-LDISP: Estimate 0.2 km Ref: 0

Transverse dispersivity - WZ-TDISP: Estimate 0.066 km Ref: 0

Vertical dispersivity - WZ-VDISP: Estimate 0.0005 km Ref: 0

Value must be greater than or equal to 0

Figure 11. MEPAS aquifer model user interface.

Once the soil texture is selected in the soil class tool or is entered on the composition screen, the total porosity and dry bulk density are automatically filled in for the characteristics screen. However, the user can enter user-specified values if desired. If pH is entered by using the soil class tool, it too shows up on the characteristics screen. Effective porosity must be entered by the user and is equal to or less than the total porosity. A help file will provide suggested values of effective porosity as related to soil texture. As effective porosity decreases, the pore water velocity increases. However, the retardation factor also increases, which can cause the constituent front velocity to decrease.

The Darcy velocity is the most sensitive input parameter affecting output of the aquifer model (Dortch et al. 2009 and 2010). The Darcy velocity must be input by the user, but the HGCT within TREECS can be used to help in estimating it.

The thickness of the aquifer moderately affects aquifer model output (Dortch et al. 2010). This parameter must be input by the user. Site characterization data should contain information regarding the depth to groundwater and the aquifer thickness or depth to bedrock.



## Concentration Locations

Tier 1 aquifer model only allows a single receptor well location for each AOI application. However, Tier 2 will allow multiple receptor well locations. The longitudinal, lateral, and vertical distances from the AOI to each receptor well location must be input by the user. The three distances are illustrated in Figure 5. The longitudinal distance  $x$  is the distance from the center of the AOI to the well in the down-gradient direction of groundwater flow. The lateral distance  $y$  is the perpendicular distance from plume center-line to the well, and the vertical distance  $z$  is the depth from the water table surface to the well intake. To ensure conservative groundwater concentration predictions, zero values can be used for  $y$  and  $z$ .

Longitudinal, transverse, and vertical dispersivity are also required input, but the model's user interface can estimate these values for the user if the user clicks the *Estimate* button on the user input screen. Usage location (well) distances and dispersivities must be input for each usage location, or well. As before, the user can select the units of input for distance and dispersivity.

There is a Flux Location tab and input screen in the user interface for groundwater discharge to surface water. There will only be one usage location in TREECS for fluxes. The flux location is where the groundwater discharges to surface water. The user must enter the longitudinal (horizontal) distance from the center of the AOI to the surface water body where it is believed that groundwater flow leaves the aquifer and enters surface water. It is possible that the target water body (where MC concentrations will be evaluated) may be further downstream of the location of groundwater discharge to surface water. This is allowed, but there will be no MC routing, losses or attenuation between the point of groundwater discharge and the target water body. In other words, the MC mass flux leaving the aquifer enters directly into the target water body even when the target water body is downstream of the groundwater discharge influent location. Like the Concentration Locations (i.e., well locations) input screen, the three dispersivities must be entered, but they can be estimated by the model user interface. The user can change the units for distance and dispersivity.

### Constituent Properties

These constituent property inputs are the same as those discussed under the vadose zone model. It should be recognized that  $Kd$  and half-life values can be different for groundwater compared with surface soil and the vadose zone. The OM content of aquifer soils is usually much lower than that of surface soils and possibly the vadose zone, thus potentially lowering the  $Kd$ . Some constituents degrade more slowly in groundwater than in soil. Others, like RDX, degrade more rapidly under anaerobic conditions, and groundwater can be anaerobic.

### Output

Output of the MEPAS aquifer model consists of the following time series at specified locations that are available via the FRAMES viewers:

- Aquifer WFF water flux ( $\text{m}^3/\text{yr}$ ) in the groundwater flow at the flux location for groundwater discharge to surface water or at the first receptor well if there is no groundwater discharge to surface water
- Aquifer WFF MC mass flux ( $\text{g}/\text{yr}$ ) associated with groundwater plume for each MC at the flux location for groundwater discharge to surface water, or at the first receptor well if there is no groundwater discharge to surface water
- Aquifer WCF (water concentration file) groundwater concentration ( $\text{mg}/\text{L}$ ) for each MC at each receptor well

### Surface Water Model – RECOVERY

The input parameters required by the RECOVERY surface water model are listed in Table 4. The inputs are divided into categories according to the input screens of the user interface. There are six input screens with the first one shown in Figure 12. In most cases, the parameter name/symbols shown in the table are the symbols used in the documentation report (Ruiz and Gerald 2001); otherwise, brief names were created for the table. The units shown in the table are the standard units for model input. The user must adhere to these units since RECOVERY does not allow for input unit conversions like the MEPAS models do.

Table 4. RECOVERY surface water model input parameters.

Parameter Name	Units	Description
Inputs Passed from soil Model or Plus-SG Operator		
WFF (surface water) water flux	m <sup>3</sup> /yr	Water flow rate from AOI soil runoff, interflow, and groundwater discharge to surface water, which are combined via the Plus-SG Operator (This flow is provided but not actually used by the RECOVERY model.)
WFF (surface water) mass flux	g/yr	Combined mass fluxes exported from AOI soil due to rainfall ejected pore water runoff ( $F_r$ ), soil erosion ( $F_e$ ), and solid phase particle erosion ( $F_{es}$ ), and interflow. This mass flux can also include groundwater mass flux due to groundwater discharge to surface water. Particulate and dissolved fluxes are included in the Surface Water WFF, where the dissolved fluxes include surface runoff (including interflow), dissolved portion of soil erosion mass flux, and aquifer dissolved fluxes which are combined by the Plus-SG Operator. The particulate flux is due to the particulate portion of the soil erosion mass flux plus the solid phase mass erosion. The RECOVERY model combines particulate and dissolved fluxes into a total mass loading for model calculations.
Surface Water Morphometry and Hydrology		
$S_w$	mg/L	Total suspended solids concentration in the water column
$f_{oc \text{ water}}$	Fraction	Weight fraction carbon in solids in water column
$A_w$	m <sup>2</sup>	Long term average water surface area
Water depth, $H_w$	m	Long term average of surface water mean depth
$Q$	m <sup>3</sup> /yr	Average annual water flow through rate
Residence time, $\tau_w$	yr	Surface water residence time
Mixed Sediment Layer		
$L$	m	Total sediment bed depth to be modeled
$z$	m	Depth of mixed sediment layer
$A_m$	m <sup>2</sup>	Mixed sediment layer surface area
$\phi_m$	Fraction	Mixed sediment layer porosity
$\rho_p \text{ mixed layer}$	g/cm <sup>3</sup>	Mixed sediment layer particle density or specific gravity
$f_{oc \text{ mixed layer}}$	Fraction	Mixed sediment layer weight fraction carbon in solids
Deep Sediment Layers		
$\phi_s$	Fraction	Deep sediment porosity
$\rho_p \text{ deep sediment}$	g/cm <sup>3</sup>	Deep sediment particle density or specific gravity
$f_{oc \text{ deep sediment}}$	Fraction	Deep sediment weight fraction carbon in solids
System Properties		
$U_w$	m/sec	Mean wind speed
Enhance diffusion	cm <sup>2</sup> /sec	Enhanced diffusion between mixed sediment layer and deep sediment
Enhanced mixing depth	cm	Enhanced mixing depth between mixed sediment layer and deep sediment

Parameter Name	Units	Description
$V_s$	m/yr	Suspended solids settling rate
$V_b$	m/yr	Deep sediment burial rate
$V_r$	m/yr	Mixed layer sediment resuspension rate
Constituent Properties		
$C_{w0}$	$\mu\text{g/L}$	Initial contaminant concentration of constituent in water
$W$	kg/yr	Additional constant external loading rate of constituent
$C_{m0}$	mg/kg	Initial constituent concentration in mixed sediment
$C_{s0}$	mg/kg	Initial constituent concentration in deep sediment
$D_m$	$\text{cm}^2/\text{sec}$	Molecular diffusivity in water of constituent
$H_e$	$\text{atm}\cdot\text{m}^3/\text{g}\cdot\text{mole}$	Henry's Law Constant of constituent
$MW$	g-mole	Molecular weight of constituent
$K_{ow}$	$(\text{mg}/\text{m}^3 \text{ octanol})/(\text{mg}/\text{m}^3 \text{ water})$	Constituent octanol-water partition coefficient
$K_{dw}$	L/kg	Partition coefficient for the water column for inorganic constituents
$K_{dm}$	L/kg	Partition coefficient for the mixed sediment pore water for inorganic constituents
$K_{ds}$	L/kg	Partition coefficient for the deep sediment pore water for inorganic constituents
$k_w$ dissolved	1/yr	Decay rate for dissolved contaminant in water
$k_m$ dissolved	1/yr	Decay rate for dissolved contaminant in mixed layer
$k_s$ dissolved	1/yr	Decay rate for dissolved contaminant in deep sediment
$k_w$ particulate	1/yr	Decay rate for particulate contaminant in water
$k_m$ particulate	1/yr	Decay rate for particulate contaminant in mixed layer
$k_s$ particulate	1/yr	Decay rate for particulate contaminant in deep sediment
Model Control Parameters		
$T$	years	Total period of simulation
$N$ print 1	dimensionless	Number of time steps between print intervals for output
$N$ print 2	dimensionless	Number of time steps between print intervals for sediment layer output
$N$ layers print	dimensionless	Number of sediment layers to plot in output

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MORPHOMETRY AND HYDROLOGY

Import data from an existing RECOVERY data file for use under ARAMS/Frames: Browse...

**WATER**

Choose one of the external loading options below.

☒ Steady State ☐ Time Varying

Suspended Solids Concentration (mg/L)  Ref: 0

Weight Fraction Carbon in Solid  Ref: 0

Enter 3 of the following values and press Recalculate Button to calculate the 4th value

Water Surface Area (m<sup>2</sup>)  Ref: 0

Water Depth (m)  Ref: 0

Flow Through (m<sup>3</sup>/yr)  Ref: 0

Residence Time (years)  Ref: 0

Calculated Residence Time (years)  Recalculate

Help References Save Back Next Exit

Figure 12. RECOVERY surface water model user interface, first screen of six.

### Inputs Passed from the Soil Model or Plus-SG Operator

The only output passed from the soil that will be used by RECOVERY is the Water Flux File (WFF) for Surface Water time series of mass flux exported from soil to surface water and from groundwater discharge to surface water. The soil mass fluxes are passed from the soil model in the form of the surface water WFF, which has adsorbed (particulate) and dissolved fluxes. The particulate flux is the combination of soil MC mass losses due to soil particle erosion (the particulate portion of erosion) and solid phase constituent particle erosion. The dissolved flux from soil is due to rainfall induced ejection of pore water and its runoff, the dissolved portion of erosion flux, and soil interflow. The Plus-SG Operator consumes and combines surface water WFF and aquifer WFF to produce surface water WFF (for both particulate and dissolved portions) which is consumed by RECOVERY. Thus, the discharge of groundwater dissolved constituent to surface water is added to the dissolved mass flux of the soil model WFF. The distinction of WFF dissolved and particulate flux is required for compliance with the FRAMES WFF specifications. The RECOVERY model combines the particulate and dissolved loadings into a single total loading for compliance with RECOVERY model specifications. The Plus-SG Operator is discussed further in Chapter 8.

The RECOVERY model requires the average annual water flow rate  $Q$  through the water body. The soil model provides an average annual runoff flow rate (including interflow), but this flow rate may be quite different from the flow moving through the water body due to runoff from other drainage basins in addition to drainage from the AOI. Thus, it is better for the user to have to provide the value for  $Q$  based on site-specific circumstances. If the AOI provides the only drainage comprising  $Q$ , then the user can estimate  $Q$  by multiplying the AOI average annual runoff rate by the AOI area and adding the interflow rate to this flow. The interflow rate is the excess infiltration times the AOI area as discussed in Chapter 8. The model does not require the MC concentration associated with water entering the water body via the water body through-flow. If there is a background loading of MC due to through-flow, then that loading can be included in the Addition Constant External Loadings field of the constituent properties screen of the RECOVERY user interface. The MC load from the AOI automatically enters the water body via the surface water WFF file that RECOVERY consumes.

### Surface Water Morphometry and Hydrology

The total suspended solids concentration of the water column ( $S_w$ ) is a required input although model results are relatively insensitive to this input. The value for  $S_w$  should be the long-term average concentration. The fraction by weight of organic carbon of the suspended solids ( $f_{oc}$  water) is a required input. The water column  $f_{oc}$  is the ratio of water column particulate organic carbon (POC) to total suspended solids (TSS or  $S_w$ ). TSS is the sum of inorganic suspended solids (ISS) and volatile suspended solids (VSS), and POC is approximately 0.4 VSS. Water column  $f_{oc}$  values can vary widely depending on the sediment delivery from the watershed and the productivity of the water body. Based upon a brief review of observed POC and TSS data for Chesapeake Bay<sup>1</sup> where extensive research results are readily available, values of water column  $f_{oc}$  varied from below 0.01 to more than 0.15, and typical values were roughly 0.05. Freshwater systems should have similar values.

Three of the following four variables must be entered by the user: surface area of the water,  $A_w$ ; mean water depth,  $H_w$ ; flow rate through the water body (i.e., flushing flow rate),  $Q$ ; and water residence time,  $\tau_w$ . These four variables are related as follows,

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<sup>1</sup> Personal communication with Dr. Carl Cerco, Research Hydrologist, Environmental Laboratory, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

$$\tau_w = \frac{A_w H_w}{Q} \quad (67)$$

Surface water flow-through or flushing rates  $Q$  can be estimated from the product of the catchment basin area that drains into the surface water body and the estimated average annual runoff depth. Procedures for calculating average annual runoff depth are available within the HGCT. Also, the estimated mean flow velocity in the water body can be multiplied by the mean cross-sectional flow area to obtain  $Q$ . The water body flow through rate should represent the combined flows from AOI runoff, groundwater discharge, plus all other sources of runoff not associated with the firing range or AOI.

### **Sediment Mixed Layer**

The definitions of  $L$  and  $z$  are diagrammed on the second input screen as shown in Figure 13, where  $z$  is the depth of the mixed layer, and  $L$  is the total sediment depth being modeled for contamination. There are model layers below  $L$ , but those layers are assumed to be clean or have no contamination initially. A typical value for  $z$  is about 0.07 m with a range of roughly 0.05 to 0.2 m. A reasonable value for  $L$  is 1.0 m, although the mixed sediment layer concentrations, which are important ecologically, are not very sensitive to the depth of  $L$ .

The mixed sediment layer surface area ( $A_m$ ), porosity ( $\phi_m$ ), specific gravity or sediment particle density ( $\rho_p$ ), and  $f_{oc}$  must be entered by the user. A good assumption is to set  $A_m$  equal to  $A_w$ . A reasonable value for mixed layer porosity is 0.7, although higher values (e.g., 0.9) are possible and generally result in lower mixed layer contaminant concentrations. Thus, 0.7 is a conservative value. A good value of specific gravity for most sediment is 2.65. The mixed layer  $f_{oc}$  is the ratio of mixed layer POC concentration and dry sediment bulk density, and it is generally less than  $f_{oc}$  of the water column. A typical range of mixed layer  $f_{oc}$  is from less than 0.01 to up to about 0.10 or 0.15. Values for New Bedford Harbor varied from a maximum of 0.134 in the inner harbor to a minimum of 0.001 in the middle and outer harbor (Abdelrhman et al. 1998).

### **Deep Sediment Layers**

Similar to the mixed layer, the user must enter on the third input screen (which is not shown here) the porosity, specific gravity, and  $f_{oc}$  for the deep

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MORPHOMETRY AND HYDROLOGY

Water

Mixed Sediments

Deep Contaminated Sediments

Clean Sediments

z

L

L = Contaminated Sediments Depth (m)  Ref: 0

z = Depth of Mixed Sediments Layer (m)  Ref: 0

MIXED SEDIMENTS LAYER

Mixed Sediments Layer Surface Area (m<sup>2</sup>)  Ref: 0

Porosity  Ref: 0

Particle Specific Gravity  Ref: 0

Weight Fraction Carbon in Solid  Ref: 0

Help References Save Back Next Exit

Figure 13. Second input screen of the RECOVERY user interface.

sediments. The main difference between screens 2 and 3 is that sediment vertical profiles can be input for the parameters of the deep sediments. Consequently, a constant value for all deep sediment layers can be entered for each, or values can be entered for each layer of the deep sediments for each of the three parameters. A typical value for porosity in deeper sediments is about 0.5. A good value for specific gravity is 2.65 as before. The deep sediment  $f_{oc}$  is generally less than the mixed layer value.

### System Properties

System properties are entered on the fourth input screen, which is not shown here. Model results are not very sensitive to wind speed since most range constituents are not very volatile. Average wind speeds are on the order of 6 m/sec for the U.S. (Dortch et al. 2009).

The two enhanced mixing parameters are in the model to emulate the effects of bioturbation. However, in most applications, it is reasonable to set both parameters to zero.



Two of the three sedimentation rate parameters ( $v_s$ ,  $v_b$ , and  $v_r$ ) must be entered, and the third parameter is set to 0 and will be computed by the model user interface using a steady-state solids balance (Ruiz and Gerald 2001). The settling rate ( $v_s$ ) is usually the easiest one to estimate and is generally on the order of 30 to 100 m/yr for fine grain sediment. If the resuspension rate is not estimated, it could be assumed to be very small (e.g.,  $1E-10$  m/yr or practically zero), and the burial rate can be set to 0 and will be calculated. Resuspension is usually fairly small for deeper, slowly moving waters that are wind-sheltered, such as small lakes and ponds.

### Constituent Properties

Constituent properties must be entered on the fifth input screen for each MC being modeled. The button labeled “Next Compound” at the top of the screen should be clicked to advance to each MC for inputs (see Figure 14).

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Previous Compound      **CADMIUM Properties**      Next Compound

Initial Concentration in Water (micrograms/L)    0.0000    Ref: 0

Inflow Concentration (micrograms/L)    0.0000    Ref: 0

Additional Constant External Loadings (kg/year)    0.0000    Ref: 0

Initial Concentration in Mixed Sediments (mg/kg)    0.00000000E+00    Ref: 0

Initial Concentration in Deep Sediments (mg/kg)    0.00000000E+00    Ref: 0

Deep Sediments Concentration Profile

Molecular Diffusivity (cm<sup>2</sup>/sec)    2.0000E-06    Ref: 0

Henry's Constant (atm-m<sup>3</sup>/gmole)    0.00000000    Ref: 0

Molecular Weight    112.0000    Ref: 0

Octanol-Water Partition Coeff. (mg/m<sup>3</sup> Octanol)/(mg/m<sup>3</sup> Water)    0.0000    Ref: 0

For contaminants with an Octanol-Water partition coefficient of zero, partition coefficients can be specified by clicking on the "View Calculated Data" button.    View Calculated Data

**DECAY COEFFICIENTS (1/yr)**

Dissolved Contaminant:			Particulate Contaminant:		
In Water	0	Ref: 0	In Water	0	Ref: 0
In Mixed Layer	0	Ref: 0	In Mixed Layer	0	Ref: 0
In Deep Sediments	0	Ref: 0	In Deep Sediments	0	Ref: 0

Help    References    Save    Back    Next    Exit

Figure 14. Properties input screen of the RECOVERY user interface.

The first five inputs are actually constituent initial and loading conditions rather than properties. For most TREECS applications, these four inputs ( $c_{w0}$ ,  $W$ ,  $c_{m0}$ , and  $c_{s0}$ ) will be set to zero, which are the default values in the user interface. These zero inputs mean that there is no contamination in the water or sediment of the water body initially, and there are no constant external loadings (such as atmospheric deposition, background load from through-flow, or point source discharges). If there is an initial contamination of MC, values for sediment and water concentrations should be entered. Sediment concentrations are much more important than water column since the water column concentrations are flushed out quickly, relative to the sediment. Likewise, if there are constant background loadings of MC or other constant external loadings, such as atmospheric deposition, those can be entered as well. There is also the time-varying loading due to the AOI export, and these loadings are included as they will be automatically passed from the soil model to the surface water model via the WFF as discussed in the section on Inputs Passed from the Soil Model. There can also be a loading due to groundwater discharge to surface water, in which case the Plus-SG operator combines the soil model WFF with the aquifer WFF as explained in Chapter 8.

The constituent properties  $D_m$ ,  $H_e$ ,  $MW$ , and  $K_{ow}$  will be passed from the constituent database if values are in the database. Inorganic constituents, such as metals, should not have database values for  $H_e$  and  $K_{ow}$ . A zero value for Henry's constant will be used in those cases, and volatilization flux will be zero. The  $K_{ow}$  value is used by the RECOVERY model to compute  $K_{oc}$  from  $K_{oc} = 0.617 K_{ow}$ , and  $K_d = f_{oc} K_{oc}$  for organic MC.

Sediment and water partitioning coefficients will have to be entered for inorganic constituents. These can be entered by clicking the "View Calculated Data" button on the Properties screen of the user interface as shown in Figure 14 and Figure 15. Three  $K_d$  values must be entered for these cases, one each for water column ( $K_{dw}$ ), mixed sediment layer ( $K_{dm}$ ), and deep sediment layers ( $K_{ds}$ ). Selecting appropriate  $K_d$  values for metals can be difficult since they are affected by the local geochemistry. In general,  $K_{dw}$  and  $K_{dm}$  should be about the same and can be much lower than  $K_{ds}$  due to the presence of sulfides in deeper, anaerobic sediments that can bind with metal cations forming insoluble precipitates. Values of  $K_d$  used for lead and copper in the Fort A.P. Hill application of TREECS Tier 1 were 4,000 and 600 L/Kg, respectively (Dortch et al. 2010).

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CADMIUM Properties

CALCULATED DATA

Fraction dissolved in the water column (Fdw)

Fraction particulate in the water column (Fpw)

Fdpm = Ratio of contaminant concentration in the mixed layer sediment pore water to total contaminant concentration in total mixed layer sediment

Fdps = Ratio of contaminant concentration in the deep layer sediment pore water to total contaminant concentration in total deep layer sediment

Mass transfer velocity between water and sediment (Vd) (cm/s)

PARTITION COEFFICIENTS

Partition coefficient for the water column (Kdw) (L/kg)  Ref: 0

Partition coefficient for the mixed sediment pore water (Kdm) (L/kg)  Ref: 0

Partition coefficient for the deep sediment pore water (Kds) (L/kg)  Ref: 0

Volatilization Rate (1/yr)

The volatilization rate is computed by

$$k_v = F_{dw} \frac{V_v}{z_w}$$

where  $F_{dw}$  = dissolved fraction in water column,  $V_v$  = a volatilization transfer coefficient (m/yr), and  $z_w$  = depth of the water column, m.

Help References

Figure 15. Calculated data and partitioning coefficients input screen of the RECOVERY model interface.

Six different decay or degradation rates ( $\text{yr}^{-1}$ ) can be entered for each constituent. These six rates are for dissolved and particulate phases for the three media (water column, mixed sediment layer, and deep sediments). For conservatism, the default values are zero. Decay rates can be computed from half-lives (see Equation 66). Decay rates are not well known for many organic constituents, so if the values are set above zero, sensitivity should be conducted to obtain a range of expected results. Decay rates for most inorganic constituents, such as metals, should be zero.

### Model Control Parameters

Model control parameters are entered on the sixth and final input screen, which is not shown here. The total period of simulation should be set long enough for the sediments to respond to changes in export loadings from soil. For example, if the operational period of the firing range is 50 years, then the surface water model simulation period should be set to at least 100 years. Sediment contaminant concentrations will decrease over decadal

time scales following cessation of range use. The number of time steps between print intervals should be set about 20 or more. The value only affects the quality of the output concentration versus time plots. The same is true for *N print 2* except that this parameter is used for deep sediment animations (concentration profiles in sediment over time) rather than concentration versus time plots like *N print 1*. The number of layers to plot is also used for the deep sediment animations. Each layer is 1.0 cm, so if the deep sediment of interest is 0.5 m deep, *N layers print* should be set to 50.

## Output

The output of the RECOVERY model includes the following for each MC, which are viewable via a special viewer developed for RECOVERY:

- Water column total (particulate plus dissolved) concentration,  $\mu\text{g/L}$ , versus time
- Surficial (mixed layer) sediment total concentration on a sediment mass basis,  $\text{mg/kg}$ , versus time
- Surficial sediment pore water dissolved concentration on a water volume basis,  $\text{mg/L}$ , versus time
- Volatilization flux from water,  $\mu\text{g/yr}$ , versus time
- Dissolved mass flux between sediment and water column,  $\mu\text{g/m}^2\text{-yr}$ , versus time
- Time animation plots of deep sediment concentration profiles over depth for
  - Total concentration on a sediment mass basis,  $\text{mg/kg}$
  - Total concentration on a sediment volume basis,  $\mu\text{g/m}^3$  and  $\text{mg/L}$
  - Dissolved concentration per volume of pore water,  $\text{mg/L}$

In addition to the RECOVERY viewer, there are three general types of FRAMES viewers that will provide output results. These include:

- SCF (Sediment Concentration File) graphical view – time series of surficial (mixed layer) sediment total concentration on a sediment mass basis ( $\text{mg/kg}$ ) and surficial sediment dissolved concentration on a water volume basis (pore water concentration,  $\text{mg/L}$ )
- WCF graphical view – time series of water column total concentration ( $\text{mg/L}$ ) and dissolved concentration ( $\text{mg/L}$ )
- WFF graphical view – time series of water column particulate (adsorbed) mass flux ( $\text{g/yr}$ ) and dissolved mass flux ( $\text{g/yr}$ ) associated with flow of water with constituents through the water body

## Surface Water Model – CMS

Only one surface water model can be used for each AOI application; thus, the model will be either RECOVERY or CMS, depending on the type of water body. The input parameters required by the CMS surface water model are listed in Table 5. The inputs are divided into categories according to the input screens of the user interface. There are five input screens with the first one shown in Figure 16. However, when operating within TREECS, the last input screen for Loading Data will not need user inputs since loadings will be automatically passed via the WFF from the soil model. In most cases, the parameter name/symbols shown in the table are the names and symbols used in the documentation report (Fant and Dortch 2007); otherwise brief names and symbols were created for the table. The units shown in the table are the standard units for model input. However, like the MEPAS models, the user can use different units, and the model user interface automatically converts them to model-standard units.

### Inputs Passed from the Soil Model or Plus-SG Operator

Similar to RECOVERY, CMS consumes a surface water WFF. However, unlike RECOVERY, CMS uses both the water fluxes and mass fluxes in the WFF, whereas RECOVERY only uses the mass fluxes, or loads. The water fluxes are added in the CMS to the constant background flow rate. The model also allows background loadings in addition to the loadings imported via the WFF. Like RECOVERY, CMS combines WFF particulate and dissolved mass loadings into a single total loading for model calculations. If there is groundwater discharge to surface water when using CMS, then the Plus-SG Operator consumes and combines surface water WFF and aquifer WFF to produce surface water WFF which is consumed by CMS, just like what is done for RECOVERY.

### Model Parameters

The user has the option of inputting either the number of computational segments or the length of each segment. Whichever is used, the other variable is computed for use in the model based upon the distance to the usage (or receptor) location of interest. Typically it is good to have at least 20 segments in a study reach.

Table 5. CMS surface water model input parameters.

Parameter Name	Units	Description
Inputs passed from soil model or Plus-SG Operator		
WFF (surface water) water flux	m <sup>3</sup> /yr	Water flow rate from AOI soil runoff, interflow, and groundwater discharge to surface water, which are combined via the Plus-SG Operator (This flow is used by the CMS.)
WFF (surface water) mass flux	g/yr	Combined mass fluxes exported from AOI soil due to rainfall ejected pore water runoff ( $F_r$ ), soil erosion ( $F_e$ ), and solid phase particle erosion ( $F_{es}$ ), and interflow. This mass flux can also include groundwater mass flux due to groundwater discharge to surface water. Particulate and dissolved fluxes are included in the Surface Water WFF, where the dissolved fluxes include surface runoff (including interflow), dissolved portion of soil erosion mass flux, and aquifer dissolved fluxes which are combined by the Plus-SG Operator. The particulate flux is due to the particulate portion of the soil erosion mass flux plus the solid phase mass erosion. The CMS combines particulate and dissolved fluxes into a total mass loading for model calculations.
Model Parameters		
Number of segments	NA	Number of computational segments in the modeled stream reach
Segment length	m	Length of each computational segment
$\Delta t$	day	Model time step
$T_p$	yr	Total period of time for the simulation
$D_x$	m <sup>2</sup> /day	Longitudinal dispersion coefficient
TSS	mg/L	Total suspended solids concentration in the water column
$h$	m	Depth of the active benthic sediment layer
$\rho_s$	g/L	Dry sediment particle density
$\phi$	fraction	Sediment porosity
$f_{oc \text{ water}}$	fraction	Fraction organic carbon in solids (water column)
$f_{oc \text{ sediment}}$	fraction	Fraction organic carbon in solids (sediment)
$T$	deg C	Water and sediment mean temperature
$W$	m/sec	Mean wind speed at 10 m above surface
Hydraulic Parameters		
$X$	km	Usage location, i.e., distance downstream from the upstream boundary to the location of interest
Geometric option	NA	Select option of either entering stream width and depth or entering cross-sectional area
$B$	m	Stream constant top width for option of entering stream width and hydraulic depth
$H$	m	Stream constant hydraulic depth for option of entering stream width and hydraulic depth
Cross-sectional area option	NA	For option of entering cross-sectional area, includes option of either entering a constant value for cross-sectional area or entering a function related to flow rate

Parameter Name	Units	Description
A	m <sup>2</sup>	Constant cross-sectional area of the flow for option of entering cross-sectional area
a	NA	Parameter in the function $A = aQ^b$ for option of entering a function for cross-sectional area as related to flow
b	NA	Parameter in the function $A = aQ^b$ for option of entering a function for cross-sectional area as related to flow
c	NA	Parameter in the function $H = cA^d$ for option of entering a function for hydraulic depth as related to flow cross-sectional area
d	NA	Parameter in the function $H = cA^d$ for option of entering a function for hydraulic depth as related to flow cross-sectional area
Q	m <sup>3</sup> /yr	Constant background stream flow rate (e.g., annual mean flow) at the head of the reach (without any flow from the AOI)
Constituent Parameters		
C <sub>i</sub>	mg/L	Constant constituent background concentration in stream at the head of the reach
C <sub>bi</sub>	mg/kg	Initial constituent concentration in the sediment bed
k <sub>dw</sub>	day <sup>-1</sup>	Decay rate of dissolved phase in water column
k <sub>pw</sub>	day <sup>-1</sup>	Decay rate of particulate phase in water column
k <sub>db</sub>	day <sup>-1</sup>	Decay rate of dissolved phase in sediment bed
k <sub>pb</sub>	day <sup>-1</sup>	Decay rate of particulate phase in sediment bed
K <sub>ow</sub>	ml/ml	Constituent octanol-water partition coefficient
K <sub>dw</sub>	L/kg	Constituent sediment-water partition coefficient in water column
K <sub>db</sub>	L/kg	Constituent sediment-water partition coefficient in sediment bed
k <sub>v</sub>	m/day	Constituent volatilization rate
V <sub>d</sub>	m/day	Constituent mass transfer rate across the sediment-water interface resulting from diffusion of dissolved constituent
MW	g/g-mol	Constituent molecular weight
D <sub>m</sub>	cm <sup>2</sup> /sec	Constituent molecular diffusivity in water
H <sub>e</sub>	atm-m <sup>3</sup> /g-mol	Constituent Henry's law constant
Sedimentation Parameters		
V <sub>s</sub>	m/day	Suspended sediment settling rate
V <sub>b</sub>	m/day	Bed sediment burial rate
V <sub>r</sub>	m/day	Bed sediment resuspension rate

**Model Parameters**

Specify one of the following:

- ☒ Number of Computational Segments: 20 Ref: 0
- ☐ Length of Each Computational Segment: 0 m Ref: 0

Time step: 0.01 yr Ref: 0

Total simulation time: 10 yr Ref: 0

Longitudinal Dispersion Coefficient: 10000 m<sup>2</sup>/day Ref: 0

Total suspended solids concentration at point of entry: 500 mg/L Ref: 0

Depth of Active Sediment Layer: 0.2 m Ref: 0

Dry Sediment Density: 2650 g/L Ref: 0

Sediment Porosity: 0.5 Ref: 0

Fraction Organic Carbon in Solids (Water Column): 0.02 Ref: 0

Fraction Organic Carbon in Solids (Sediment): 0.02 Ref: 0

Temperature (deg C): 20 Ref: 0

Wind Speed at 10m above Surface: 5 m/s Ref: 0

Figure 16. CMS surface water model user interface, first screen of five.

The user sets the model time step and the total simulation time. For long-term (decades and longer) simulations, the time step should be made as large as possible to reduce run time without compromising accuracy. For this reason, it is a good idea to make runs using various time step sizes and comparing results. For long-term simulations, 0.1 to 0.2 years is a reasonable time step size to consider. For short-term simulations, such as a month or less, much shorter time steps should be used. The total simulation time is used to define how long of a period the model is run. The simulation time should be long enough for the water body to respond to the changes in loading conditions and to capture study needs. For example, if the intent is to capture conditions during range use and years following it or future long-term range use, then simulations could require 50 to 100 years.

The longitudinal dispersion coefficient is used to account for longitudinal mixing associated with the limitations of a one-dimensional assumption. Dispersion accounts for constituent spreading along the channel due to



channel bottom velocity shear across the channel and channel irregularities. Fischer et al. (1979) recommend the following equation for estimating longitudinal dispersion  $D_x$  (m<sup>2</sup>/sec) in natural river channels,

$$D_x = 0.011 \frac{U^2 B^2}{H u_*} \quad (68)$$

where

$U$  = mean flow velocity in the channel for the given flow, m/sec

$B$  = channel top width at the water surface for the given flow, m

$H$  = hydraulic depth of flow, m, where the product  $UHB$  is the flow discharge rate

$u_*$  = shear velocity of the flow, m/sec

The shear velocity can be approximated from  $0.1U$ . The dispersion coefficient should be estimated for the annual average flow rate (discharge) in the stream.

The user must enter the TSS concentration for the stream. The version of CMS used in TREECS will maintain a constant TSS concentration over time and throughout the reach. This version does not allow the option to conduct suspended solids transport as the stand-alone version does.

The active sediment layer represents the upper horizon of the sediment bed that is fairly well-mixed and exchanges with the water column. A typical value is on the order of 10 cm to 20 cm.

The dry sediment density is typically 2650 g/L (2.65 g/cm<sup>3</sup>). Porosity of the active layer can vary from about 0.5 to 0.9. A reasonable value is 0.7, but if the sediment layer is thicker than 20 cm, then a lower value for porosity should probably be used. The guidance provided for fraction of organic carbon within the RECOVERY model section applies here too. The mean water and sediment temperature and mean wind speed should represent annual averages if long-term simulations are being conducted.

### Hydraulic Parameters

The user enters the distance downstream to the usage (receptor) location of interest. This is the location where the concentrations must be known to

assess impacts on receptors. Multiple locations can be assessed in the stand-alone version of CMS, but the TREECS version will be limited to only one usage location to reduce system development complexity. Only one location will usually be needed anyway for surface water.

As shown in Figure 17, the user has the option of entering either the stream width and hydraulic depth or the flow cross-sectional area. If the first option is selected, then the reach-average channel top width and hydraulic depth should be entered for the average annual flow conditions. If the cross-sectional area is selected, then the user has the option of entering a single constant area for the entire reach or entering parameters to compute the reach area and depth, given the flow, which can change over time due to the water fluxes (which can be time-varying) being consumed from the WFF. However, for TREECS, only annual average hydrology is used presently, thus the flows in the WFF are constant. For this reason, there is no reason to use the second option for cross-sectional area. The user must enter the stream flow rate  $Q$  at the point of entry (or background flow) where external loadings (such as runoff from AOI) are entering, which is the beginning of the modeled stream reach. As stated above, this background flow does not vary in time.

Figure 17. The Hydraulic Parameters user input screen of CMS.

## Constituent Parameters

Constituent parameters must be entered for each modeled constituent on the constituent parameters screen, which is not shown here. The user must enter the background stream concentration, which is the concentration in the stream at the head of the reach before mixing with the AOI loading. Typically, this value can be set to zero unless there is a known background concentration. The initial concentration of MC in the sediment bed must be entered. However, it may be set to zero in many applications since this input can have little significance for long-term simulations with continuing loadings since the initial bed concentration will eventually change over time to reflect the loadings. However, if the user is not conducting a long-term analysis with continuing loadings and needs to input initial concentrations in sediment and water, he or she may do so. There is no input for initial water concentration since streams are usually flushed rather quickly of any initial conditions for the water column.

The four decay rates can be set to zero for conservative predictions of constituent fate. Alternatively, the user can input rates for dissolved and particulate constituent phases for both the water column and the sediment bed. Little guidance can be provided for values to use since rates can vary widely among constituent chemicals, as well between water and sediment and particulate and dissolved. The assumption is often made that the particulate phase constituent does not decay, while dissolved phase does. Some chemicals may decay faster in the water column than in the bed, while others behave the opposite. It is noted that decay, or degradation, in this model includes all loss types (biodegradation, photolysis, hydrolysis, and oxidation) except volatilization, which is a separate process as in the RECOVERY model. The decay rate for metals is usually set to zero.

The user has the option of choosing either to input the Octonol-water partition coefficient, which is used by the user interface to compute  $K_d$  for organic chemicals, or input the  $K_d$  for the water column and sediment bed. The second option should be chosen for non-organic constituents, such as metals, but can also be used for any constituent if the user has better information on  $K_d$ . If a value for  $K_{ow}$  is in the constituent database and that option is selected, that value is automatically passed to the input field for this parameter. The model computes  $K_d$  when  $K_{ow}$  is provided using the same methods as described for the RECOVERY model.

The user can either have the user interface compute the rate parameters for volatilization and dissolved phase mass transfer between water column and bed, or the user can input these two rates. The methods for these calculations are described by Fant and Dortch (2007), and all of the information required for the calculations is contained within the interface input.

Values for the three chemical-specific properties, molecular weight, molecular diffusivity in water, and Henry's law constant, are automatically passed from the constituent database if values are present. Otherwise, the user must enter the missing values.

### **Sedimentation Parameters**

Similar to the RECOVERY model, the version of CMS in TREECS requires the user to enter two of the three sedimentation parameters, settling rate, burial rate, and resuspension rate, and the remaining unspecified parameter is computed from a steady-state solids balance. The three rates are constant throughout the study reach and over time. It is usually easier to estimate the settling and resuspension rates for rivers. The user must ensure that a positive burial rate is computed. Estimation of settling and resuspension rates is beyond the scope of this report, but there is a large body of knowledge regarding the estimation of these parameters. Settling rate can be estimated from TSS mean particle size and Stokes law. Estimation of resuspension rates is discussed by Fant and Dortch (2007).

### **Output**

The output of the CMS includes the following for each MC, which are viewable via a special viewer developed for CMS:

- Water column total or dissolved concentration (mg/L) versus stream length for given times
- Time animation of water column total or dissolved concentration (mg/L) versus stream length
- Bed sediment total concentration on a sediment mass basis (mg/kg) versus stream length for given times
- Time animation of bed sediment total concentration on a sediment mass basis (mg/kg) versus stream length
- Water column total or dissolved concentration (mg/L) versus time for given distances along the stream

- Distance animation of water column total or dissolved concentration (mg/L) versus time
- Bed sediment total concentration on a sediment mass basis (mg/kg) versus time for given distances along the stream
- Distance animation of bed sediment total concentration on a sediment mass basis (mg/kg) versus time

In addition to the CMS viewer, there are three general types of FRAMES viewers that will provide output results. These include:

- SCF (Sediment Concentration File) graphical view – time series of bed sediment total concentration on a sediment mass basis (mg/kg) and bed sediment dissolved concentration on a water volume basis (pore water concentration, mg/L)
- WCF graphical view – time series of water column total concentration (mg/L) and dissolved concentration (mg/L)
- WFF graphical view – time series of water column particulate (adsorbed) mass flux (g/yr) and dissolved mass flux (g/yr) associated with the constituents in the stream flow

## 8 Other Considerations

There are several additional features that merit discussion. These features include: soil interflow and groundwater discharge to surface water; fate of mixtures; fate of degradation products; sensitivity and uncertainty, and modeling fate of water miscible constituents. Each of these features is discussed below as well as plans for how each will be handled in TREECS Tier 2.

### Soil Interflow and Groundwater Discharge

#### Interflow

Interflow through the vadose zone or soil to surface water is a minor pathway in most cases, but it could be a potential pathway for surface soils having a high hydraulic conductivity with an impermeable or semi-impermeable soil layer at a shallow soil depth, thus creating a perched water table. Since the TREECS Tier 1 and 2 models are based on average annual hydrology, interflow must be added through specification of the fraction of average annual infiltration that is lost to interflow before entering the vadose zone model. Interflow is caused by infiltration flow that is greater than the maximum percolation rate (i.e., groundwater recharge rate) of the vadose zone layer, which is the saturated hydraulic conductivity,  $K_s$ . A conceptual schematic of flow within the soil, vadose, aquifer system is shown in Figure 18. After prompting the user to enter a value of  $K_s$  for the vadose zone layer, the soil model user interface will automatically provide an estimate of the interflow fraction as follows. If the soil infiltration rate,  $q_w$ , is less than or equal to  $K_s$ , the fraction of interflow,  $F_{if}$ , is estimated to be zero. If  $q_w$  is greater than  $K_s$ , then  $F_{if} = \frac{q_w - K_s}{q_w}$ . The user can also inter

his/her own estimate for  $F_{if}$ . In many cases, the interflow fraction should be set to zero, which will send all of the infiltration water to the vadose zone and aquifer models.

No fate processes, such as sorption or degradation, are applied to the interflow flux. Thus, the fraction of interflow will be multiplied times the infiltrating flow rate and mass fluxes computed by the soil model to produce the interflow water flow rate and mass fluxes. These values will then be added to the surface runoff flow rate and dissolved mass fluxes

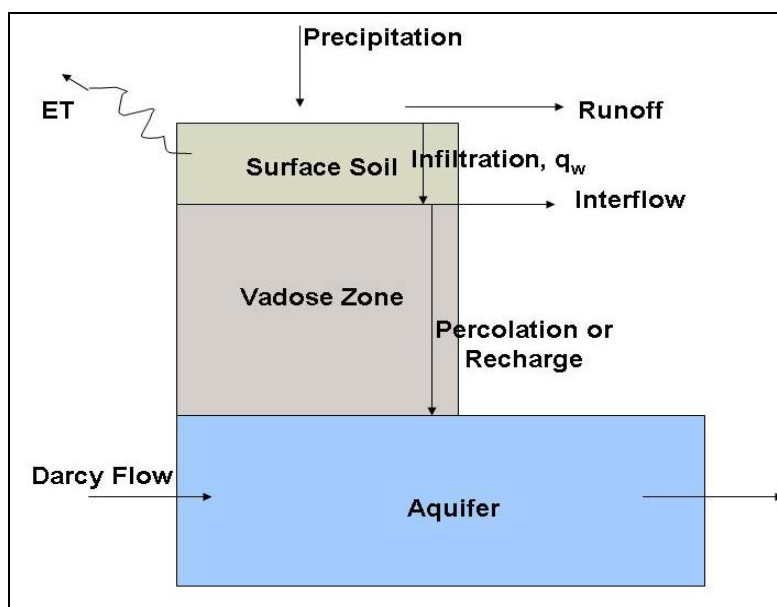


Figure 18. Conceptual schematic of surface and sub-surface hydrology.

computed by the soil model, and the combined results will be written to the WFF surface water. The soil model must also reduce the water flow and mass fluxes to vadose zone by the same amount before writing to the WFF vadose file.

### Groundwater Discharge

During dry seasons when surface stream flows are low, groundwater discharge can contribute a major portion of the stream flow. For some watershed conditions, groundwater discharge can be the primary contributor to flow in small streams. For these reasons, it is necessary to include a contribution of MC loading from groundwater flow in surface water.

A module must be developed to provide groundwater discharge to surface water. The new module will consume the MEPAS Aquifer water flux file (WFF) which contains aquifer flow ( $\text{m}^3/\text{yr}$ ) and aquifer mass flux ( $\text{g}/\text{yr}$ ) at a flux location, which is specified in the MEPAS Aquifer model user interface. The flux location in this case should be the distance from the center of the AOI to the point in the landscape where the stream or water body and aquifer have crossed in the landscape. If the target surface water point of interest (i.e., receptor target location) is further downstream, then there are no further mass losses or mass flux attenuation as water travels from the point of groundwater intersection to the water body target location.

Since the receiving surface water body models within TREECS are designed to receive surface water runoff and fluxes from the AOI soil, the new module must also be able to combine surface and aquifer water flux files (WFFs) into a combined surface water WFF. A Plus operator was developed for ARAMS that allows one to combine multiple WFFs into one, but the WFFs had to be of the same type, such as aquifer or surface water. The reason for this is that the surface water WFF contains mass flux for dissolved and adsorbed mass flux, whereas the aquifer WFF contains only dissolved mass flux.

The new module must serve two functions. It must perform an operation on the aquifer WFF for groundwater discharge to surface water, and it must allow combining of surface water and aquifer WFFs. The new module is referred to here as the Plus operator for Surface water and Groundwater, or Plus-SG for short.

The Plus-SG module should have a brief user interface that will request the user to input the groundwater flow rate entering the receiving surface water body. The flow rate input units can vary, but the flow rate will be converted to  $\text{m}^3/\text{yr}$  to be consistent with WFF specifications. The groundwater discharge to surface water will be assumed to be constant over time, which is fairly consistent with base flow conditions in small streams. The Plus-SG module will divide the aquifer WFF mass flux by the aquifer WFF flow at the flux location to obtain an aquifer concentration at the location of groundwater discharge to surface water. This concentration will be multiplied by the user-input groundwater discharge rate to obtain values for mass flux ( $\text{g}/\text{yr}$ ) from groundwater to surface water. The water flux rate will be the constant value of groundwater discharge to surface water input by the user.

The groundwater discharge water and mass fluxes must be combined with the surface water WFF. The surface water WFF dissolved mass fluxes that enter the Plus-SG will be combined with the groundwater-to-surface-water mass flux to obtain a total dissolved mass flux entering the water body. The surface water WFF particulate (adsorbed) mass fluxes that enter the Plus-SG will be passed unaltered to the Plus-SG output WFF, which will be consumed by the water body. The surface water WFF water flux will be combined with the groundwater-to-surface-water flow to obtain the total flow entering the water body. Thus, the Plus-SG operator will output a WFF that is similar to the surface water WFF, except that surface water



and groundwater-to-surface-water and mass fluxes have been combined. This output file will be consumed by the surface water models.

The existing Plus Operators are able to handle time series with different time points when combining fluxes and flows. This feature must be preserved in the Plus-SG module.

The RECOVERY model uses only the WFF mass flux or load (g/yr) as input; water flux from WFF is not used. Since the RECOVERY model assumes a fully mixed water column, it does not matter that the mass fluxes for surface water and groundwater are combined. The user must enter a water body flow through rate in the model user interface since other water sources could enter. This flow rate should represent the combined flows from AOI runoff, groundwater discharge, and other sources of runoff not associated with the firing range or AOI.

The CMS uses both the WFF load and water flux (flow rate) as input. The CMS does not presently have a feature to allow for flow distribution along the river reach, as might occur with groundwater discharge. Thus, all of the flow from AOI surface water runoff and groundwater enter at the head of the modeled reach. The user can also input a constant background flow, which is flow entering the head of the reach before the flows from AOI runoff and groundwater discharge are added. Consideration should be given to adding a distributed flow feature in the future for groundwater discharge.

## **Fate of Mixtures**

Some MC can exist in mixtures, such as several HE, including Composition (Comp) B, Octol, and Tritonal, which are mixtures of RDX and TNT, HMX and TNT, and TNT and aluminum, respectively. Mixtures can affect the dissolution of individual constituents within the mixture.

Taylor et al. (2009a) found that for Comp B, the dissolution rate of less soluble RDX controlled the dissolution rate of more soluble TNT. The TNT dissolution rate was essentially the RDX dissolution rate times the initial bulk RDX/TNT mass ratio. However, initially, the dissolution rates of RDX and TNT were about the same without the mass ratio multiplier. As discussed in Appendix B, the TREECS dissolution model accurately predicted Comp B, RDX, and TNT dissolution masses using the solubility of the mixture and the respective mass fractions of the mixture, suggesting

that the solubility of the mixture could be the proper approach for applying the TREECS dissolution model.

Taylor et al. (2009a and 2009b) found that the dissolution rate of the TNT in Tritonal occurred at the pure TNT dissolution rate as if the aluminum flakes had no influence. However, the AF fitting parameter in their model had to be reduced from 2 for pure TNT to 1.22 for Tritonal, or nearly by half as discussed in Appendix B. If the solubility of TNT is reduced by half, the TREECS dissolution model also matches the observed TNT dissolution results fairly well, which is also discussed in Appendix B. Taylor et al. (2009a) found that the dissolution rate of less soluble HMX did not fully restrain the dissolution rate of TNT for Octol, where TNT dissolution occurred at a rate between the independent TNT and HMX controlled rates.

The above discussion suggests that the mechanisms for dissolution of mixtures is still not well understood and merits further study. Additionally, MC residue can occur as a result of munitions that use both pure explosive components and mixtures, such as pure RDX and Comp B. The MIDAS database does not provide information on munitions mixtures, such as the amount of Comp B; rather, it only provides the mass of each explosive component, such as RDX and TNT. As a result the amount of mixture residue may not be known or could be difficult to estimate. To account for mixtures, it is also necessary to conduct a mass balance on each mixture residue in addition to the pure constituent mass balances. These limitations and requirements make it difficult to model the fate of mixtures. Inclusion of mixtures at this time could result in delays in delivering an initial TREECS Tier 2 capability. Therefore, it is recommended that explicit treatment of mixtures not be included in Tier 2 at this time, but this capability should be a consideration for future versions.

Accordingly, all MC will be assumed to be in pure form, and the dissolution rates will be computed with Equations 40-43 using pure constituent properties. This may not be a bad assumption for the less soluble constituents if their dissolution rate really controls the dissolution rate for mixtures. This is a conservative assumption for the more soluble constituents since they will be predicted to dissolve faster than could actually occur for mixtures, thus promoting their mobility in water systems. Should mixtures be included in future versions of TREECS, it is recommended at this time that the solubility of the mixture be used for the dissolution modeling if that solubility can be estimated.

## Fate of Degradation Products

The degradation (or daughter) products of some MC, such as TNT, can pose more concern than the parent compound. The fate of each daughter product of concern should be tracked through each media. This requires modeling the fate and transport of both parent MC and daughter products within each medium model where the source of the daughter product is the degradation flux of the parent constituent. Presently, the TREECS system and several of the models (soil and surface water) do not provide the means to model degradation products. Providing such a capability will require extensive development and modifications. Thus, the initial versions of TREECS will not have this capability, but this extension is recommended for future versions.

## Sensitivity and Uncertainty

The capability to assess parameter and input sensitivity and output uncertainty (S/U) will be included in Tier 2, but not Tier 1, of TREECS. This capability will utilize modules and specifications that exist within ARAMST<sup>TM</sup>. The unaltered FRAMES S/U module within ARAMST<sup>TM</sup> will be used in Tier 2 for setting up inputs for the assessment. The methods are based on Monte Carlo simulation using Latin Hypercube sampling of random inputs. The user specifies the type of distribution (such as normal, log normal, etc.) and the distributions statistics for each declared uncertain input. The output can be sampled to provide the occurrence frequency of specific measures, such as peak concentration, or to provide uncertainty confidence bands on output measures, such as concentration time series.

## Modeling Fate of Water Miscible Constituents

Some MC may be water miscible or easily and quickly dissolved in water, such as perchlorate constituents. There was a question of whether the Tier 2 soil model would be able to handle the very rapid dissolution that occurs with such highly soluble MC. In such cases, the dissolution flux  $F_{dis}$  in Equation 2 rapidly approaches the MC loading rate  $L$ , the solid phase erosion flux  $F_{es}$  rapidly approaches zero, and the solid phase mass  $M_s$  is small. Thus, water miscible MC mostly exists as non-solid phase mass  $M_{ns}$ . Several constituent properties are no longer important for miscible MC, including initial solid phase concentration, initial particle diameter  $d_{sm}$  and solid phase particle mass density  $\rho_{sm}$ . Tests were run to determine the response of the Tier 2 soil model for miscible MC.

A spreadsheet version of the Tier 2 soil model was applied for a case of water miscible MC using potassium perchlorate as the MC, which has a solubility of about 20,000 mg/L. The initial particle diameter was set to 500  $\mu\text{m}$ . The spreadsheet model used a first-order accurate Euler time integration scheme to solve the differential equations. With a time step of 0.01 years, the model did not converge on a correct solution. With a time of 0.001 years, the model did properly converge to values fairly close to the correct answers. For smaller initial particle diameters, dissolution was faster, so smaller time steps were required to keep a stable solution.

The Tier 2 soil model was also programmed using the Visual Basic language with two numerical solution options. One option is the regular fourth-order Runge-Kutta integration method, which uses a constant time step. The other option is the adaptive Runge-Kutta-Fehlberg (Press et al. 1996) integration method, which allows the time step to adjust as necessary to maintain a stable solution. The programmed model was run for the same test case of perchlorate as was run for the spreadsheet version with an initial particle diameter of 500  $\mu\text{m}$ . With a constant time step of 0.01 years, the model ran to a stable, but incorrect solution. With a constant time step of 0.001 years, the model ran to a stable and correct solution with nearly the same results as the spreadsheet model. The model was also run with the auto-time-stepping option. That run converged to the correct solution without having to know the time step required for a valid solution. However, when the model was run with an initial particle diameter of 1.0  $\mu\text{m}$  and with auto-time-stepping, the model had much difficulty finding a small enough time step to complete the run.

Given the potential stability and accuracy problems noted above, it was decided that a miscible MC feature must be added to the Tier 2 soil model. An additional input variable is needed to declare if an MC is miscible. If an MC is miscible, then the dissolution flux  $F_{dis}$  is set equal to the loading flux  $L$  for each time step during the model solution. Additionally, the calculations for particle diameter  $d_{sm}$  and particle specific surface area  $\alpha$  are not required for miscible MC, and the solid phase erosion flux  $F_{es}$  should be zero. Inputs for initial particle diameter, initial solid phase concentration, and particle density are not required for miscible MC. Testing of the miscible MC feature showed that the above changes worked very satisfactorily without any stability or accuracy issues.

## 9 Summary

TREECS Tier 2 assessment methods will require more detailed site data, and will require more knowledge and skill to apply than Tier 1, but Army environmental staff that has a cursory understanding of multi-media fate and transport should have no problem applying Tier 2. The Tier 2 approach will allow time-varying analyses with solid phase dissolution and system losses, such as degradation and volatilization. Such analyses should provide more accurate predictions with generally lower receiving media concentrations due to mediating effects of transport phasing/dampening and natural attenuation/degradation. Tiers 1 and 2 focus on contaminant stressors and human and ecological health end point metrics. This report describes the approach and formulations that will be used for Tier 2 of TREECS.

Like Tier 1, Tier 2 addresses impact areas of interest and does not consider firing points at this time. Also like Tier 1, Tier 2 will compare forecasted media concentrations against protective human and ecological health benchmark concentrations. Receiving media include groundwater, surface water, and surface water sediments. Additionally, Tier 2 uses average annual hydrologic input like Tier 1. However, Tier 2 should be more accurate than Tier 1 for assessing MC fate, especially for metals, since the time domain and dissolution are included. Tier 2 should be used when Tier 1 indicates that a protective health benchmark will be exceeded.

The Tier 2 approach for TREECS is based on solving mass balance equations for MC mass that evolves over time. The soil model assumes that a single homogeneous layer or soil compartment represents the AOI with spatially uniform properties and MC concentrations. However, MC residue loadings to soil and computed soil MC mass, concentrations and fluxes (losses, gains, and exports) can vary over time. Including time as a dimension, which was not included for Tier 1, allows consideration of both solid and non-solid phase MC mass with dissolution of the solid phase transferring mass to the non-solid phase. The non-solid phase mass consists of aqueous dissolved, aqueous adsorbed-to-soil, and gas or vapor in air components. Equilibrium portioning among the non-solid components is assumed, which collapses the non-solid mass balance into a single differential equation. Thus, the Tier 2 soil model solves two ordinary

differential equations, one for solid phase and one for the non-solid phase mass balance.

Tier 2 receiving media models consist of the MEPAS vadose zone model, MEPAS aquifer model, RECOVERY surface water model, and CMS surface water model. Both surface water models include benthic sediments. MC mass can move from soil to vadose zone, and from vadose zone to aquifer. MC mass can also move from soil to surface water. The user decides which surface water model to use, either RECOVERY or CMS. MC mass can move as interflow from the soil compartment to surface water where interflow is the excess infiltration that cannot percolate through the vadose zone. There are no mass losses or gains associated with the interflow. Additionally, MC mass can move from groundwater to surface water. The initial version of Tier 2 will not allow MC mass to move from surface water to surface water, such as transport from a stream to a lake, although this feature could be added later if necessary. The RECOVERY model is better suited for modeling standing or pooled water, such as lakes, ponds, wetlands, etc, whereas the CMS is better suited for modeling flow in streams and rivers, including tidal rivers.

The MC residue mass loading model is described. The residue mass loading model takes munitions use information and develops mass loadings for each MC. The MIDAS database is used to establish the amount of MC within each munitions type. Sources of MC residue within the loading model include unexploded mass for high-order and low-order detonations and sympathetic detonation of duds. Corrosion and release of MC inside duds is not considered at this time. The number of rounds fired per year must be entered for each munitions item used. Estimates of yield percentages for low-order, high-order, and sympathetic dud detonations and occurrence percentages of duds, low-order detonations, and sympathetic dud detonations must be entered.

The fate formulations within the Tier 2 soil model are developed and presented, and each of the receiving media fate models is described as well. The input requirements for each fate model are presented and information for obtaining inputs is provided. The output from each fate model is also defined.

Some in-depth study and analysis were required for establishing appropriate mathematical descriptions for several fate processes, including

dissolution, volatilization, and solid phase particle erosion. Each of the processes can be quite complex. A simplified volatilization formulation provides reasonable flux estimates without requiring a more complex model of depth-varying soil properties and concentrations. A generic dissolution formulation is developed that is relatively easy to apply and does not require calibration parameters. The dissolution formulation agrees with previous formulations and field measurements. Bed load formulations were explored for describing solid phase MC erosion. The Einstein and Brown formulation seemed to perform favorably for estimating soil erosion, and it can probably be applied for mixtures of soil and solid phase MC. However, a much simpler approach is recommended for Tier 2 which is based on the USLE. The Einstein and Brown approach may be more appropriate for short-term, storm-event modeling of MC fate.

A Plus-SG Operator module must be developed to allow import fluxes of both surface water erosion/runoff and groundwater discharge into receiving surface water. This operator will combine the two types of fluxes after requiring that the user input the groundwater discharge flow rate.

The fate of mixtures is affected by the dissolution rate of mixtures, which still remains a topic for further research. Proper modeling of mixtures requires conducting mass balances on each mixture mass, as well as mass balances for each constituent in the mixture. The mixture mass residue loading rates onto the range must also be known or estimated. This requires knowing which mixtures are contained in munitions. The MIDAS database does not provide this information; rather, it provides the mass of each constituent or explosive pure component. Therefore, dissolution of mixtures will not be implemented into Tier 2 at this time although this feature should be considered for future versions of TREECS.

The capability to simulate the fate of degradation products also will not be implemented into Tier 2 at this time. This feature will require additional development for the soil model as well as extensive modifications to the TREECS system and the receiving water models. Such development would preclude the release of Tier 2 during the funding cycle of the present TREECS project. This capability should be considered for future versions of TREECS.

Tier 2 will consider only one initial particle size for solid phase MC. The Tier 2 soil model will compute the time evolution of the single particle size,

which affects the time-varying dissolution rate. Particle size also affects the solid phase particle and soil mixture erosion rate if a bed load type function is used for erosion. The inclusion of multiple particle sizes requires conducting a mass balance on each particle size class for each MC. This feature would also require input of the distribution of initial solid phase particle sizes for each MC. Including multiple solid phase particle sizes substantially increases the input data requirements and modeling requirements; thus, this feature should be considered carefully before deciding to implement it for future versions of TREECS.

The capability to assess parameter and input sensitivity and output uncertainty (S/U) will be included in Tier 2, but not Tier 1, of TREECS. This capability will utilize modules and specifications that exist within ARAMST<sup>TM</sup>. The output can be sampled to provide the occurrence frequency of specific measures, such as peak concentration, or to provide uncertainty confidence bands on output measures, such as concentration time series. The S/U module uses Monte Carlo simulation with Latin Hypercube sampling.

The Tier 2 soil model will handle miscible MC, such as perchlorate that dissolves rapidly in water, without any special consideration. However, the adaptive time step integration scheme should be the default method for the final programmed Tier 2 soil model in TREECS.

The TREECS advisory panel expressed an interest in the development of an additional TREECS tool for assessing single storm events and first flush MC concentrations in streams. This feature was not included in this initial version of Tier 2 in TREECS. However, it is feasible to add this feature sometime in the future.



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## Appendix A: Solid Phase MC Particle Erosion

It is feasible for solid phase MC particles to erode with soil during rainfall events, washing into streams and traveling to target water bodies. In fact, results of laboratory studies (Larson et al. 2004 and 2005) indicate that particulate lead in runoff is a major pathway for lead migration from firing range soils. However, these studies did not determine whether the particulate lead was soil adsorbed aqueous phase or solid phase lead particles. Additionally, laboratory studies of erosion may not reflect the true nature of what happens in the field where overland flow and eroded material must travel much greater distances.

Soil adsorbed aqueous phase transport is already taken into account in the Tier 2 soil model as described in Chapter 4. Solid phase MC erosion was identified as a potential pathway in Chapter 4, but methods for computing it were not defined. Various sediment transport formulations were reviewed in an attempt to find a way to describe the process of solid phase MC particle erosion. This process is quite complex since the size and specific gravity of soil and MC particles can affect the erosion rate. Thus, it is possible that the properties of the mixture of soil and MC determine erosion rates, depending on the quantity of MC in the soil.

Julien (1995) presents various methods for estimating bed load transport in channels. The methods were reviewed, and two methods (Duboy's equation and the Einstein and Brown equations) were evaluated to explore their potential use. The two methods were applied to hypothetical conditions as well as laboratory data presented by Larson et al. (2004). Although the details of the two methods and their application results are not presented here, the general conclusions drawn are described below.

### Duboy's Equation

The Duboy's equation is stated as,

$$q_{bv} = \frac{0.173}{d_s^{0.75}} \tau_o (\tau_o - \tau_c) \quad (A1)$$

where

- $q_{bv}$  = volume of bed material load per unit width, ft<sup>2</sup>/sec  
 $d_s$  = particle diameter, ft  
 $\tau_o$  = shear stress of the flow, lb/ft<sup>2</sup>  
 $\tau_c$  = critical shear stress for particle movement, lb/ft<sup>2</sup>

The shear stress of the flow can be estimated from the product  $\gamma hS$ , where  $\gamma$  is the specific weight of water (62.4 lb/ft<sup>3</sup>),  $h$  is the depth of flow, and  $S$  is the surface slope. The difficulty with the DuBoy's equation, and other similar methods involving the critical shear stress, is estimating the critical shear stress. This estimation is difficult enough for pure soil or sediment particles, but the complexity is compounded with a mixture of soil and MC particles, where the MC particles can have much different particle sizes and specific gravity. For example, the specific gravity of lead is 11.35 compared to 2.65 for most soils. Typical particle sizes for lead fragments from a firing range are on the order of hundreds of micrometers (microns, 10<sup>-6</sup> m) (Larson et al. 2005) compared to 64 microns or less for fine sand and other fine soil material.

There are formulae for estimating the critical flow velocity  $u_c$ , such as the following equation suggested by Julien (1995) with  $u_c$  in units of ft/sec,

$$u_c = 1.4\sqrt{(G-1)gd_s} \quad (A2)$$

where,

- $G$  = specific gravity of the particle  
 $g$  = acceleration due to gravity, 32.2 ft<sup>2</sup>/sec

With the critical flow velocity, the critical shear stress can be estimated. The approach that was adopted for estimating  $u_c$  for a mixture was to calculate the specific gravity and average particle size for the mixture taking into account the average particle sizes and the specific gravities of the soil and MC particles and the fraction by weight of the MC in the soil.

The Duboy's equation was tested and results compared with those computed with the Modified Universal Soil Loss Equation (MUSLE) for soil only (no MC). The comparison was relatively close. Next the Duboy's equation was applied to laboratory studies reported by Larson et al. (2004). The laboratory studies consisted of boxes tilted at 0.0625 slope filled with metal-contaminated soil and exposed to controlled rainfall for a period of

16 weeks. Runoff and leachate from each box (i.e., lysimeter or test cell) were periodically collected and analyzed for dissolved and total metals, as well as total suspended solids (TSS). The average total runoff of soil mass from all of the eight test cells at the end of the 16 weeks was 165 g. Duboy's equation was applied to the conditions of the laboratory experiments. The shear stress computed for the laboratory conditions was  $1.0\text{E-}4$  lb/ft<sup>2</sup>, which is much less than the computed critical shear stress for the soil of 6.88 lb/ft<sup>2</sup>. Thus, zero erosion was computed. This was the case even for pure soil with no metal content. Further examination of the Duboy's equation revealed that results are extremely sensitive to the value of the critical shear stress, where the value had to be very close to but slightly less than the value of the flow shear stress in order to get the observed amount of soil erosion. It was concluded that a method was needed that did not require estimation of the critical shear stress.

One of the interesting points of the measured laboratory data is that the concentration of lead in the runoff was about 1.1 percent of the sediment concentration, which is close to the initial soil concentration of lead, which was 8100 mg/kg, or 0.81 percent lead. This could be a coincidence, but it could mean that lead particles are eroding as a mixture with the sediment. It could also mean that small lead particles are dissolving and adsorbing to small sediment particles that are being eroded.

## Einstein and Brown Equations

The Einstein and Brown equations do not require estimation of a critical shear stress. The equations are not repeated fully here and can be found in the text by Julien (1995). There is a non-linear relationship for dimensionless volumetric unit sediment discharge ( $q_{bv*}$ ) versus the dimensionless Shields parameter  $\tau_*$ . The variable  $q_{bv*}$  is defined as

$$q_{bv*} = \frac{q_{bv}}{\omega_o d_s} \quad (\text{A3})$$

where  $\omega_o$  is Rubey's clear-water sediment fall velocity, an equation for which is presented by Julien (1995) that is dependent on soil grain size and specific gravity. The dimensionless Shields parameter is defined as

$$\tau_* = \frac{\tau_o}{(\gamma_s - \gamma) d_s} \quad (\text{A4})$$

where  $\gamma_s$  is the specific weight of sediment, and all other variables have been previously defined. There are three non-linear equations used to relate  $q_{bv*}$  to  $\tau_*$  depending on the value of  $\tau_*$ .

Application of the Einstein and Brown equations to the laboratory conditions yields a cumulative soil erosion of 0.2 g, which is three orders of magnitude smaller than the measured soil erosion amount of 165 g. However, the value of the Shields parameter for the laboratory study was less than reported field values, thus outside the range of values used to develop the relationships.

The Einstein and Brown equations were also applied to conditions at Fort A.P. Hill, VA. Fort A.P. Hill was a proof-of-concept test case for the TREECS Tier 1 models (Dortch et al. 2010). The average annual runoff estimated for Fort A.P. Hill of 0.067 m/yr was used for the calculations to test the Einstein and Brown equations. The soil erosion computed with the Einstein and Brown equations was 30 tons/acre-yr, compared with 54 tons/acre-yr as computed with the Universal Soil Loss Equation (USLE). Thus, it appears that the Einstein and Brown equations hold some promise for computing soil erosion at field scales.

The good traits about the Einstein and Brown equations are that they do not require a critical shear stress. They are dimensionless -- results will vary with runoff flow rate and soil conditions -- and they include variables that could be used to describe characteristics of sediment and MC mixtures. The particle specific gravity, specific weight, and size, can be adjusted to reflect a mixture. The fraction by weight of soil and MC can be used to adjust these variables by assuming spherical particles.

## Recommendations

It is recommended that detailed bed load transport equations for sediment-MC mixtures not be used in Tier 2 at this time. If the user wants to consider erosion of solid phase particles, then such an option should be included in Tier 2, but the calculation should be based solely on results of the USLE that is already needed for soil erosion that exports aqueous phase (adsorbed and dissolved) MC. This will mean that solid phase MC will not affect the overall soil erosion; rather, it will be considered as part of the soil erosion. The laboratory results discussed above indicate that



this may not be a bad assumption. It is anticipated that inclusion of this term will be for sensitivity assessment in most cases.

In this case, the solid phase erosion export flux,  $F_{es}$  (g/yr), can be computed from

$$F_{es} = f_{MC} \rho_b A E \quad (A5)$$

where,

$f_{MC}$  = fraction by weight of solid phase MC mass to soil mass

$\rho_b$  = soil dry bulk density, g/m<sup>3</sup>

$A$  = AOI site area, m<sup>2</sup>

$E$  = soil erosion rate as determined from the USLE, m/yr

It is recognized that  $f_{MC}$  can be computed from

$$f_{MC} = \frac{M_s}{AZ_b \rho_b} \quad (A6)$$

where  $M_s$  (g) is the solid phase MC mass in the AOI, and  $Z_b$  (m) is the thickness of the surface soil layer. Plugging Equation A6 into A5 yields

$$F_{es} = M_s \frac{E}{Z_b} \quad (A7)$$

Equation A7 resembles Equation 23 for  $F_e$  after recognizing that concentration is mass divided by soil volume ( $AZ_b$ ). If the user elects to include solid phase MC erosion, then the additional flux term  $F_{es}$  will be computed from Equation A7 and subtracted from the right side of the solid phase mass balance equation as noted in Equation 2. The export flux  $F_{es}$  will be added to the particulate mass flux of the WFF to import into the receiving water model. If this option is not selected, then  $F_{es}$  will be set to zero.

Preliminary testing of the Tier 2 soil model for a constant source loading of RDX was performed with  $F_{es}$  included using Equation A7 to compute it. Testing with 1,000 micron particles indicated that the mass export due to this term can be about the same order of magnitude as the export due to

rain induced pore water extraction ( $F_r$ ) and roughly two orders of magnitude greater than soil erosion of the aqueous dissolved and adsorbed phases ( $F_e$ ). For 100 micron particles, mass export due to  $F_{es}$  was about 6 times greater than that due to  $F_e$ , but export due to  $F_r$  was about 20 times greater than that due to  $F_{es}$ . Thus, including the  $F_{es}$  term can be relatively important compared with  $F_e$  but less important compared with  $F_r$ . However, the relative importance of the term depends on various factors including particle size, the erosion rate  $E$  of the site, soil partitioning  $K_d$ , and water solubility. As  $E$  increases, the relative importance of  $F_{es}$  increases.

The flux  $F_{es}$  is an additional mass loading term in the WFF file for the surface water models as noted in Table 4. However, the fact that this loading is solid phase MC mass will not be recognized by the surface water models since these models do not handle the non-aqueous phase. This extra loading will be added to the other two loadings ( $F_r$  and  $F_e$ ) and treated as part of the total aqueous phase mass loading. This means that solid phase mass will be immediately available for partitioning between sediment and water just as the non-solid phase. For HE, this is not a bad assumption since dissolution rates are relatively fast. It is also not a bad assumption for metals, since they have high sediment partitioning coefficients which tie up aqueous phase adsorbed metals in the sediments where the solid phase metals will be located, too. Thus, the sediment total concentration should not be much different whether or not the solid phase mass is treated separately.

The TREECS advisory panel expressed an interest in the development of an additional tool for assessing single storm events and first flush MC concentrations in streams. It is recommended that the Einstein and Brown equations be considered for erosion of soil-MC mixtures in the transient, event-oriented TREECS soil model if storm event capabilities are added to TREECS.

## Appendix B: Dissolution Model Comparisons

### Comparison with Outdoor Results

The dissolution formulation (Equation 40) for the TREECS Tier 2 soil model was applied to experimental results reported by Taylor et al. (2009b) for TNT to gain validation confidence. The experiments were conducted outdoors with individual cm-sized chunks of TNT and Tritonal (an 80:20 mixture of TNT and aluminum flakes) exposed to natural precipitation for one year. The 11 TNT chunks varied from 0.361 g to 1.975 g with an average mass of 0.922 g, and the five Tritonal chunks varied from 2.162 to 5.32 g with an average mass of 3.154 g. Each chunk rested on glass frits in individual glass funnels. Each funnel was connected to a 1 L glass bottle beneath the funnel so that all precipitation interacting with the chunk could be collected and analyzed. The glass bottles were set inside an insulated wooden box beneath the funnel to keep the collection in the dark to prevent photo-transformation.

The TREECS dissolution formulation was compared against the average of the 11 TNT and 5 Tritonal individual chunk dissolution results. The average of the measured dissolved TNT mass was 0.021 g for pure TNT and 0.024 g for Tritonal. However, dissolved TNT accounted for only about one-third of the total mass losses of TNT from the chunks. There was an unaccounted mass loss of 0.037 and 0.062 g of TNT for pure TNT and Tritonal, respectively. The unexpected and unaccounted mass loss was attributed to the formation and dissolution of red TNT photo-transformation products on the surface of the chunks. Thus, there is still much that is not well-known regarding TNT fate processes.

Taylor et al. (2009b) propose a linear drop impingement dissolution model for HE as follows,

$$M_{dis}(t) \approx \pi AF \bar{C}_s H(t) (a_0 + \bar{D}_{om})^2 \quad (B1)$$

where,

$M_{dis}(t)$  = particle mass loss over time due to dissolution, g

$AF$  = particle surface area factor, dimensionless

- $\overline{C}_s$  = precipitation temperature-weighted, average constituent solubility limit in water, g/cm<sup>3</sup>  
 $H(t)$  = cumulative rainfall over time, cm  
 $a_0$  = initial particle radius, cm  
 $\overline{D}_{om}$  = rainfall mass-weighted, mean raindrop diameter, cm

If Equation B1 is applied for one year, then  $H(t)$  is  $P_t$ . Total rainfall, including equivalent snowmelt, for the year was 122.7 cm. Precipitation-weighted average temperature for the year was 10.5 °C, which resulted in an average solubility of 7.1E-5 g/cm<sup>3</sup>. The value of  $\overline{D}_{om}$  was estimated to be 0.17 cm. The average of the linear model best-fit area factors  $AF$  was 2.0 and 1.22 for the pure TNT and Tritonal tests, respectively. Using the average initial masses for TNT and Tritonal of 0.922 and 3.154 g, assuming spherical particles, and using the respective solid mass densities of 1.65 and 1.87 g/cm<sup>3</sup>, the initial particle radii of TNT and Tritonal were computed to be 0.51 and 0.74 cm, respectively. Using the above values in Equation B1, the computed dissolution mass loss of TNT ( $M_{dis}$ ) is 0.025 and 0.028 g, respectively, for pure TNT and Tritonal. These values compare fairly closely with the measured dissolved TNT mass of 0.021 and 0.024 g for pure TNT and Tritonal. It is noted that the same solubility limit was used for pure TNT and Tritonal, which was inferred as the recommended approach by Taylor et al. (2009b).

The dissolution formulation proposed for the TREECS Tier 2 soil model is stated as

$$F_{dis} = P_t \alpha M_s C_s \quad (B2)$$

where,

- $F_{dis}$  = dissolution mass flux, g/yr  
 $P_t$  = average annual total precipitation, m/yr or cm/yr  
 $\alpha$  = average specific surface area of the solid phase mass, m<sup>2</sup>/g or cm<sup>2</sup>/g  
 $M_s$  = total solid phase mass remaining, g  
 $C_s$  = annual average of solubility limit in water, g/m<sup>3</sup> or g/cm<sup>3</sup>

Consistency of units must be maintained in Equation B2 as noted in the definitions of terms.

Equations B1 and B2 are quite similar after recognizing that  $F_{dis}$  and  $M_{dis}$  are equivalent, as well as  $P_t$  and  $H$ , on an annual basis. If  $C_s$  is determined from precipitation-weighting rather than time-averaging of air temperature, then it is equivalent to  $\bar{C}_s$ . The product  $\alpha M_s$  represents an average solid phase mass surface area. Thus, the only additional parameters that are in Equation B1 that are not in Equation B2 are the fitting parameter  $AF$  and the raindrop diameter. However, if the value of 2 is used for  $AF$  as was done for pure TNT, then the product of  $\pi AF$  times the quantity in parentheses in Equation B1 is approximately equal to the solid phase mass surface area for pure TNT. In this case, Equations B1 and B2 are really almost the same. Equation B2 has some added appeal of not requiring a fitting parameter  $AF$  or raindrop diameter. The raindrop diameter seems like an unnecessary parameter when considering that rainfall often pools on the ground causing rain water to totally engulf or submerge each HE particle. Thus, in real world settings, the dissolution rate may be a consequence of how rapidly rain water on the ground is replaced, i.e., the rainfall or precipitation rate, rather than the drop diameter and drop interval.

Equation B2 (i.e., Equation 40) was applied to the average of the pure TNT and Tritonal test results. In the application of Equation B2,  $M_s$  was updated (decreased) by an amount equal to the dissolution of TNT. This was accomplished by solving Equation 2 with the loading and solid phase particle erosion fluxes set to zero. However, this update did not include the additional dissolution and mass loss associated with supposed photo-transformation products. Equation 43 was used to update the average particle diameter, and Equation 42 was used to compute  $\alpha$  given the particle diameter and the solid mass density.

The application for pure TNT was rather straightforward, and the inputs were the same as those cited for the linear drop impingement model. The values used for  $C_s$  and  $\rho_{sm}$  were  $71 \text{ g/m}^3$  and  $1.65 \text{ g/cm}^3$  ( $1.65\text{E}6 \text{ g/m}^3$ ), respectively. Assuming spherical particles, this resulted in an initial particle diameter of 1.022 cm (0.01022 m) for an initial TNT mass of 0.922 g, which resulted in an initial value for  $\alpha$  of  $3.56\text{E}-4 \text{ m}^2/\text{g}$  ( $3.56 \text{ cm}^2/\text{g}$ ). Equations B2, 2, 42, and 43 were coded into a spreadsheet and solved using a first-order, Euler time integration with a time step of 0.01 yr. The computed cumulative TNT dissolved mass after one year was 0.028 g, which compares fairly well with the linear drop impingement model results of 0.025 g and the observed results of 0.021 g.

A model run was made where the remaining mass  $M_s$  was decreased each time step by 3 times the dissolution flux computed for the time step in an attempt to better represent the mass loss due to dissolution of the supposed photo-transformation products. This correction decreased the cumulative TNT dissolved mass after one year by only 0.001 g. Reducing the time step to 0.001 yr to improve numerical accuracy decreased the cumulative TNT dissolved mass after one year by only 0.0003 g. Overall, the computed result for pure TNT compares very well with the linear drop impingement model and is reasonably close to the measured TNT dissolution mass.

The application to Tritonal was less straightforward than for TNT. The input water solubility limit is less certain since Tritonal has aluminum mixed with TNT. The average initial particle diameter was set to 1.48 cm (0.0148 m) based on an initial mass of 3.154 g, spherical particles, and solid mass density of 1.87 g/cm<sup>3</sup>. The mass density was based on a ratio of 80:20 TNT and aluminum with respective mass densities of 1.65 and 2.73 g/cm<sup>3</sup>. With the initial particle diameter, the initial  $\alpha$  was computed to be 2.46E-4 m<sup>2</sup>/g (2.46 cm<sup>2</sup>/g). Using the solubility limit of TNT of 71 g/m<sup>3</sup> and without correcting the additional dissolution of photo-transformation products, the computed cumulative TNT dissolved mass (corrected for 80 percent content of TNT in Tritonal) after one year was 0.054 g, or about double the linear drop impingement model and more than double the measured value.

Another model run for Tritonal was made assuming that the total mass dissolved each time step was 3 times the TNT mass dissolved to account for the mass loss due to dissolution of supposed photo-transformation products. This correction only decreased the cumulative TNT dissolved mass by 0.001 to 0.053 g. Another model run was made assuming that the solubility limit of Tritonal was less than TNT and in proportion to the 80:20 mixture of TNT and aluminum with a zero solubility for aluminum. This assumption resulted in a solubility of 56.8 g/m<sup>3</sup>. The cumulative TNT mass dissolved after one year for the lower solubility and the corrected total mass dissolution was 0.043 g, which is still nearly double the measured value of 0.024 g. It is noted again that the parameter  $AF$  in the linear drop impingement model had to be reduced by nearly half from 2 to 1.22 for modeling Tritonal. There is no fitting parameter for the TREECS dissolution model other than trying to determine an appropriate solubility for a mixture. The relatively large initial mass of the explosive and the solubility limit are the primary variables responsible for the over-prediction.

The approach described above for Tritonal was to model the dissolution and total mass of the mixture using solubility, initial mass, and solid mass density of the mixture. The problem lies in knowing the true controlling solubility limit of a mixture. Taylor et al (2009a) found that for mixtures (such as Comp B and Octol), the constituents of lower solubility (such as RDX or HMX) can control or lower the dissolution rate for the more soluble constituents (such as TNT). They did not observe an aluminum controlled dissolution of TNT for Tritonal; rather, TNT dissolved at rate that was independent of aluminum in the mixture. The small particle drop impingement model (Taylor et al. 2009a) does not require the  $AF$  parameter, and the model matched measured dissolution mass loss very well for Tritonal over about 75 days using the solubility of TNT.

If the solubility of Tritonal is set to half of that of TNT, or 35 g/m<sup>3</sup>, the cumulative TNT mass dissolved after one year computed with the TREECS dissolution model was 0.027 g, which is close to the same result computed with the fitted linear drop impingement model. Perhaps the dissolution of TNT is eventually impeded by the presence of the aluminum flakes after a longer rainfall exposure time of a year, similar to the way less soluble RDX and HMX impede the dissolution of TNT in Comp B and Octol (Taylor et al. 2009a). Regardless of the reason for the over-prediction of TNT dissolved mass for Tritonal, it is evident that more study is required for modeling the dissolution of mixtures.

Testing of the TREECS dissolution model for HE indicated that although the particle specific surface area  $\alpha$  increases over time due to particles shrinking as dissolution occurs, the actual surface area, which is the product  $\alpha M_s$ , decreases over time because  $M_s$  is decreasing at a greater rate than  $\alpha$  is increasing. Thus, the dissolution rate flux decreases over time. This result is for the case on no additional HE loading.

### **Comparison with Laboratory Results for Comp B**

The results of a laboratory dissolution study of Comp B by Lever et al. (2005) were also used to evaluate the proposed TREECS dissolution model. Water was dropped on individual particles of Comp B, and the dissolved masses were measured in the laboratory experiments. The TREECS model (Equations B2 or 40, 2, 42, and 43) was applied for the conditions of particle 1 in the paper, which had an estimated initial Comp B mass of 1.821 mg. The initial particle diameter was computed assuming a sphere and a particle density of 1.65 g/cm<sup>3</sup>.

With a rainfall rate of 0.55 cm/hr, 1.73 mg of Comp B was measured as dissolved in 68 days with 1.09 mg of RDX and 0.64 mg of TNT dissolved in the 68 days. Using the mass ratio of RDX/TNT in the Comp B samples of about 1.72, the computed solubility limit of the mixture was 76.9 mg/L. Using the mixture solubility, the TREECS dissolution model predicted that 1.74 mg of Comp B would be dissolved in 68 days with 1.1 mg of RDX and 0.64 mg of TNT dissolved. The RDX and TNT dissolution masses are simply the Comp B dissolution mass times the respective mass fractions of each component.

If the solubility of RDX is used as suggested by Lever et al. (2005) and Taylor et al. (2009a) to control the rate of Comp B dissolution, then the TREECS model under-predicts the dissolved total mass after 68 days with only 1.41 mg dissolved, rather than 1.74 mg. If the mass and solubility of the individual constituents are used, then the dissolved mass of RDX is 0.96 mg after 68 days or is under-predicted, and the mass of TNT is predicted to be gone in 44 days, or the dissolved mass is over-predicted. Therefore, these results indicate that it is better to use the solubility of the mixture. However, as discussed in Chapter 8, there are other factors to consider before recommending modeling dissolution of mixtures in TREECS Tier 2.

## Evaluation of Dissolution Time

Equation B2 was used to estimate the length of time it would take to nearly fully dissolve a 1-cm particle of Comp B. Equation B2 can be rewritten as

$$F_{dis} = \frac{dM_s}{dt} = \gamma M_s \quad (B3)$$

where  $\gamma = P_t \alpha C_s$  and has units of  $\text{yr}^{-1}$ . Equation B3 can be solved for the time required to reach 90 percent mass loss via dissolution, resulting in

$$t_{90} = \frac{2.3}{\gamma} \quad (B4)$$

where  $t_{90}$  (yr) is the time required to reach 90 percent mass loss.

As an example, it is assumed that  $\alpha$  is constant over time for a 1-cm chunk of Comp B with a density of 1.65 g/cm<sup>3</sup> and a solubility of 40 mg/L



(corresponding to RDX), which is suggested by Taylor et al. (2009a). The chunk is assumed to be exposed to rainfall of 75 cm/yr, which is the average for the U.S. as suggested by Taylor et al. (2004). With these conditions, Equation B4 predicts that 90 percent of the Comp B chunk will dissolve in 210 years. The time should be less than 210 years since  $\alpha$  (thus  $\gamma$ ) will increase over time. In fact, the full numerical model (i.e., solution of Equations B2, 2, 42, and 43) predicts that 90 percent of the Comp B mass is dissolved in 147 years. These predictions for nearly full dissolution time are far less than those suggested by Taylor et al. (2004), which were on the order of 1,000 years or more. Given that the larger chunks of HE will tend to fragment into smaller particles over time, the complete dissolution time could be even far less than these projections. As an example, the TREECS model predicts that a 1 mm particle of Comp B exposed to 75 cm/yr of rainfall will be dissolved 90 percent in 15 years. Compared to less soluble MC, such as metals, HE particles dissolve rapidly.

Taylor et al. (2009b) used their more recent linear drop impingement model to project long-term dissolution and life spans of various sized HE particles. Their results show that it would take about 100 years to fully dissolve 1 g of TNT at an annual average temperature of 10.5 °C with an average annual rainfall of 100 cm/yr. Equation B4 predicts it would take 94 years to dissolve 90 percent of the 1 g chunk of TNT. The TREECS numerical dissolution model predicts it will take 65 years to dissolve 90 percent of the 1 g chunk of TNT and 95 years to dissolve 99 percent of it. This latter result compares closely with the 100 year projection made by Taylor et al. (2009b). As they pointed out and as can be observed from Equations B2 and B4, dissolution rate and particle life span are linearly related to precipitation rate. Thus, if the precipitation is half of the above rate, the life span will double.

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#### **14. ABSTRACT (Concluded)**

The information provided in this report is sufficient to serve as design specifications for the development of models and software that will comprise Tier 2 of TREECS. The details of the Tier 2 soil model formulations provided herein can also help serve as documentation for that model. All components will be packaged within a user-friendly PC client-based application with an emphasis on ease-of-use.